Argonne National Laboratory

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 1.   Bench-scale Investigation
of a Process for
Zirconium-Uranium Alloy Fuel

by

D. Ramaswami, N. M. Levitz,
J. T. Holmes, and A. A. Jonke

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

PART 1. BENCH-SCALE INVESTIGATION
OF A PROCESS FOR
ZIRCONIUM-URANIUM ALLOY FUEL

by

D. Ramaswami, N. M. Levitz,
J. T. Holmes, and A. A. Jonke

Chemical Engineering Division

December 1964

Other reports in this series are:

TABLE OF CONTENTS

6

LIST OF FIGURES

8

LIST OF TABLES

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 1. Bench-scale Investigation
of a Process for
Zirconium-Uranium Alloy Fuel

by

D. Ramaswami, N. M. Levitz,
J. T. Holmes, and A. A. Jonke

ABSTRACT

A fluid-bed fluoride volatility process for the re-
covery of uranium from highly enriched uranium-Zircaloy-2
and uranium-aluminum alloy fuels has been developed. The
conceptual process involves two basic chemical reaction
steps conducted in a fluid-bed reactor. In the first step, the
alloying material is separated as a volatile chloride by re-
action with hydrogen chloride. In the second step, the urani-
um is recovered as its volatile hexafluoride by reaction with
fluorine.

Process development work conducted in a $1\frac{1}{2}$-in.-
diam. nickel fluid-bed reactor with normal uranium-
Zircaloy-2 alloys showed that recovery of greater than 99%
of the uranium in the fuel can be achieved. High decontami-
nation from fission products is expected on the basis of tech-
nology developed in previous studies. Considerable economic
advantage of this process over current reprocessing schemes
appears possible because (a) small waste volumes are pro-
duced, mostly in solid form; (b) considerable flexibility in
process operating conditions exists; (c) overall fewer oper-
ations are needed; and (d) the product is uranium hexafluo-
ride, which is readily amenable for isotope separation or
conversion for reuse as fuel.

SUMMARY

A fluid-bed fluoride volatility process for the recovery of uranium
from highly enriched uranium-Zircaloy-2 and uranium-aluminum alloy
fuels has been developed. The conceptual operation of the process consists
of two steps: a hydrochlorination step, in which alloying materials are
separated by virtue of the volatility of their chlorides, and a fluorination
step, in which the uranium is volatilized and recovered as the hexafluoride.

The reactions are conducted in a bed of inert alumina granules, fluidized by nitrogen and reagent gases. The use of a fluid bed facilitates dissipation of the reaction heat. An important feature of this process is the use of a packed bed of alumina as a high-temperature filter.

In the first step, by reaction with HCl, the alloying elements of the fuel are converted into chlorides that are volatile at the reaction temperature; the uranium chlorides are relatively nonvolatile and remain in the system. Particulate uranium chlorides entrained from the fluid bed by the exit gas stream are retained by the packed-bed filter. In the recovery step, the uranium chlorides in both the fluid bed and the packed-bed filter are reacted with elemental fluorine, and the product UF_6 is recovered in cold traps maintained at dry-ice temperatures (-78.5°C).

Development work pertaining to the hydrochlorination and fluorination of uranium-Zircaloy-2 alloy is summarized in this report. The studies were carried out in a $1\frac{1}{2}$-in.-diam. fluid-bed reactor system.

Recoveries of uranium equivalent to greater than 99% of the uranium in the alloy charge were consistently achieved under a wide variety of process operating conditions. An example of the variation in the process conditions is the quantity of uranium charged which was varied by an order of magnitude (2.8 to 36.2 g as 1 to 5 w/o uranium-Zircaloy alloy). Recommended operating conditions for processing a uranium-Zircaloy-2 alloy charge are as follows:

Bed material: High-fired alumina (fused or sintered).
Fluid bed: Sufficient quantity of nominal 40 mesh alumina to cover the element (a multiplate assembly).
Packed-bed filter: -14 +20 mesh alumina, 6 in. deep.

Hydrochlorination: Temperature of fluid bed: 350 to 450°C.
Temperature of packed-bed filter: 330 to 350°C.
Time: ~8 hr per charge.
Gas velocity: 0.5 to 0.7 ft/sec in the fluid bed and the packed-bed filter (down flow of gases).
Quantity of HCl: ~2.5 stoichiometric amounts.
Concentration of HCl: 5 to 75 v/o as desired to maintain high reaction rates.

Fluorination: Gradual increase in temperature from 250 to 500°C while fluidizing with 5 to 10 v/o fluorine in nitrogen, then gradual increase in fluorine concentration to 90 v/o; the alumina may be fluidized or maintained static during the final cleanup period.
Total time: About 4 to 8 hr, depending on the quantity of uranium charge.

A hydrofluorination step of 1-hr duration at 350°C with HF concentrations of 20 to 50 v/o may be employed immediately following the hydrochlorination step to remove the bulk of the chloride before the introduction of fluorine. This step was found to have no affect on uranium recovery.

Uranium losses, consistently less than 1% of the uranium in the initial charge, were due to two sources: (1) that contained in the gas stream exiting the packed-bed filter during the hydrochlorination step, and (2) that retained by alumina at the end of the fluorination step. These uranium losses averaged ~0.04% (during hydrochlorination) and ~0.4% (retained by alumina) of the uranium in the initial fuel charge. Concentration in the beds of 0.01 w/o uranium after fluorination corresponded to this level. The high-fired alumina (both sintered and fused grades) was found to be a satisfactory inert bed material. The alumina did not agglomerate or cake and remained free-flowing and fluidizable throughout the reaction cycle.

The relative distribution of the minor constituents of Zircaloy-2 and simulated inactive fission products added with the fuel conformed with the distributions estimated from the volatilities of their higher-valent chlorides and fluorides. The distributions of fission products indicate that partial decontamination is achieved during the two reactions; further, known technology of distillation or sorption and desorption for final decontamination indicates that high decontamination can be achieved. The presence of fission-product elements and minor constituents of Zircaloy-2 did not affect the uranium recoveries.

The process, as conceived, appears to offer considerable economic advantage over current reprocessing schemes because (a) small radioactive wastes volumes are produced, mostly in solid form; (b) considerable flexibility in process operating conditions exists; (c) overall fewer operations are needed; and (d) the product is uranium hexafluoride, which is readily amenable for isotope separation or conversion for reuse as fuel. It appears that fuels decayed for a short time, or fuels with very high burnup, can be processed by this scheme.

A forthcoming report, ANL-6830 (see page 3), will outline a similar process developed for the processing of uranium-aluminum alloy fuels.

I. INTRODUCTION

In nuclear reactors for power generation, several kinds of highly enriched uranium-alloy fuels are utilized. Uranium-zirconium and uranium-aluminum alloy fuels are most widely used types. For example, highly enriched uranium-zirconium alloy fuels are used in nuclear submarines. Uranium-aluminum alloy fuels are commonly used in research and test reactors and in a variety of training reactors.

Spent forms of the highly enriched uranium-alloy fuels, as well as scrap fuel elements, require reprocessing to recover uranium for economic reasons. Currently, aqueous reprocessing methods employing solvent extraction techniques are being used to recover the enriched uranium.[1] The use of the aqueous reprocessing methods results in large volumes of liquid wastes which pose storage and handling problems. Minimization, if not elimination of the aqueous, radioactive wastes is desirable; fluidized-bed fluoride volatility techniques appear to achieve this.

Other possible advantages of fluidized-bed processes include over-all fewer operations and direct production of a desirable product form, uranium hexafluoride, which is readily amenable to isotope separation or conversion for reuse as fuel. It appears that fuels that have decayed for a short time or fuels with very high burnup can be processed by fluoride volatility techniques, whereas for aqueous processes such fuels pose a problem due to possible radiation damage to the organic solvents. These features indicate that the volatility process may have a considerable economic advantage over current aqueous reprocessing schemes.

The conceptual operation of the fluidized-bed volatility process (Figure 1) consists of two main chemical-reaction steps conducted in a single vessel. The first is a separation step, hydrochlorination, in which the alloying materials are volatilized; the second is a recovery step, fluorination, in which the uranium is volatilized and recovered as the hexafluoride. The reactions are conducted in a bed of inert alumina granules, fluidized by nitrogen and reagent gases. The use of a fluidized bed facilitates dissipation of the reaction heat. In Step 1, by reaction with HCl, the alloying elements of the fuel are converted into chlorides that are volatile at the reaction temperature. The volatile chlorides, mainly $ZrCl_4$ in the case of zirconium alloys, and $AlCl_3$ in the case of aluminum alloys, are carried out of the system and are pyrohydrolyzed to a solid oxide waste. In the overall flowsheet, the HCl is regenerated during the pyrohydrolysis operation and can be reused. The uranium forms particulate chlorides that are relatively nonvolatile and remain in the fluid-bed reactor system. Any particulate uranium chlorides entrained from the fluidized bed by the exit gas stream are filtered by a static bed of alumina. This type is used because of its simplicity and its suitability for high-temperature operation.

Figure 1

SCHEMATIC FLOWSHEET FOR REPROCESSING
URANIUM-ZIRCONIUM ALLOY FUELS

108-5290

In the recovery step, the uranium chlorides in both the fluid bed and the packed-bed filter are reacted with elemental fluorine, and the product UF_6 is recovered in cold traps maintained at dry-ice temperatures. The excess fluorine may be disposed of or may be recycled to the reactor. The UF_6 may be further decontaminated in a distillation column, or by adsorption and desorption on NaF pellets. The decontaminated UF_6 is finally returned for the production of the fuel. The manufacture of the fuel includes isotope separation and reconversion of the hexafluoride to the metal. The technology of the three final steps, decontamination, isotope separation, and production of highly enriched uranium-alloy fuel elements, was established previously.

Development work on the hydrochlorination and fluorination of normal uranium-Zircaloy-2 alloys carried out in a bench-scale fluid-bed reactor ($1\frac{1}{2}$-in. diam.) is summarized in this topical report. The development of a satisfactory reaction cycle for processing enriched alloy fuels is described in terms of the results of the individual reaction steps. The effects of operating variables on either uranium losses or uranium recovery are detailed; included are results of variations of the basic $HCl-HF-F_2$ cycle. Practical experience with packed-bed filters, an important feature of the process, is described. Since the investigation was developmental in nature, the process conditions evolved out of sequential experimentation and analyses. This report is based in part on the experimental data that were reported in the Chemical Engineering Division Summary Reports from July 1961 to December 1963.* In a forthcoming topical report, ANL-6830 (see page 3), similar process development work with normal uranium-aluminum alloys will be summarized. Pilot-plant studies, now in progress to demonstrate this fluid-bed volatility process on a practical scale (~30 kg of alloy charge), and bench-scale studies involving irradiated fuel materials, will be summarized in subsequent topical reports.

---

*ANL-6413, pp. 136 to 140; ANL-6477, pp. 144 to 148; ANL-6543, pp. 147 to 150; ANL-6569, pp. 113 to 118; ANL-6596, pp. 146 to 153; ANL-6648, pp. 152 to 169; ANL-6687, pp. 139 to 144; ANL-6725, pp. 176 to 182; ANL-6800, pp. 269 to 282.

II. LITERATURE REVIEW

The fluid-bed volatility process for the recovery of highly enriched uranium from uranium-Zircaloy-2 alloy fuels involves two main reaction steps which provide the separation of zirconium from uranium and then recovery of the uranium. Literature data on the overall reactions involved in this process are presented in Section A below. Because of the complexity of these reactions, earlier process development studies have been mainly empirical. Nevertheless, these studies are considered important contributions to the technology and are reviewed in Section B below.

A. Process Chemistry

1. Hydrochlorination. In the first step, the uranium-Zircaloy-2 alloy is reacted with HCl while submerged in an inert (alumina) fluid bed maintained at temperatures in the range 350 to 500°C. The zirconium is converted to the tetrachloride by the following reaction:

$$Zr(s) + 4HCl(g) \rightarrow ZrCl_4(g) + 2H_2(g), \qquad \Delta H^\circ_{298} = -113 \text{ kcal/mole.}$$
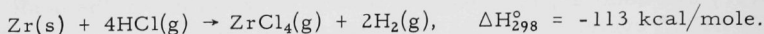
The reaction of uranium with HCl results in the formation of UCl_3 (mainly) and UCl_4, as follows:

$$U(s) + 3HCl(g) \rightarrow UCl_3(s) + (3/2)H_2(g), \qquad \Delta H^\circ_{298} = -146 \text{ kcal/mole;}$$

$$UCl_3(s) + HCl(g) \rightarrow UCl_4(s) + (1/2)H_2(g), \qquad \Delta H^\circ_{298} = -16.8 \text{ kcal/mole;}$$
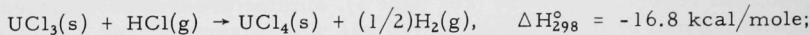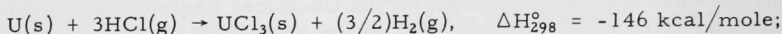
Further, HCl is strongly absorbed by UCl_3 and can only be removed in vacuum. The thermochemical data, along with physical properties of the uranium-chlorine compounds, were reported by Katz and Rabinowitch.[2]

The physical properties of $ZrCl_4$ (pressure-volume-temperature measurements) were reported by Palko et al.[3] and Nisel'son and Sokolova.[4] The sublimation point of $ZrCl_4$ at 1 atm is 331°C. The properties of HCl, along with all other gases (H_2, F_2, N_2, etc.,) used in the current work, are available in the Matheson Gas Data Book.[5] The properties of zirconium were reported by Blumenthal[6] and by Elison and Petrov.[7]

The chemical behavior of the minor constituents[8] in Zircaloy-2,* as well as that of the fission products,[9] is also of importance. The minor constituents of Zircaloy-2 and simulated fission products added to the system may form their higher-valent chlorides and oxychlorides if HCl contains oxygen as an impurity. The thermochemical properties of oxides,

---

*Zircaloy-2 is a high-zirconium alloy which contains several minor elements. A few significant minor elements are tin (1.5%), iron (0.15%), chromium (0.10%), and nickel (0.05%).

chlorides, and fluorides have been summarized by Glassner.[10] The heats of dissociation of gaseous chlorides and vapor pressure data are reported by Feber.[11]

2. <u>Hydrofluorination and Fluorination.</u> During hydrochlorination, volatile chloride products are carried out of the system by the fluidizing nitrogen; nonvolatile particulate-reaction products are retained either by the fluid bed or the packed-bed filter and are subsequently fluorinated at temperatures of 250 to 500°C. The fluorination may be conducted in two ways: a) with an $HF-F_2$ sequence, or b) with fluorine alone. The main chemical reactions involved in the two cases as seen below are different; the final product in both cases, though, is UF_6:
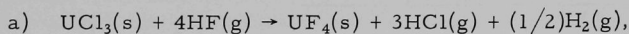
a) $\quad UCl_3(s) + 4HF(g) \rightarrow UF_4(s) + 3HCl(g) + (1/2)H_2(g),$

$\quad\quad \Delta H^o_{298} = -40.7 \text{ kcal/mole};$

$\quad UCl_4(s) + 4HF(g) \rightarrow UF_4(s) + 4HCl(g),$

$\quad\quad \Delta H^o_{298} = -43.7 \text{ kcal/mole};$

$\quad UF_4(s) + F_2(g) \rightarrow UF_6(g),$

$\quad\quad \Delta H^o_{298} = -60.0 \text{ kcal/mole};$

b) $\quad UCl_3(s) + 3F_2(g) \rightarrow UF_6(g) + (3/2)Cl_2(g),$

$\quad\quad \Delta H^o_{298} = -293 \text{ kcal/mole};$

$\quad UCl_4(s) + 3F_2(g) \rightarrow UF_6(g) + 2Cl_2(g),$
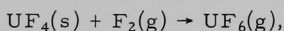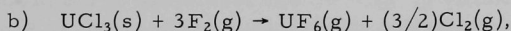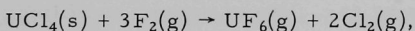
$\quad\quad \Delta H^o_{298} = -253 \text{ kcal/mole}.$

The extent of reaction between chlorine product and excess fluorine to form ClF_3 and ClF depends on the temperature:[12,13,14]

$\quad (1/2)Cl_2(g) + (3/2)F_2(g) \rightleftarrows ClF_3(g),$
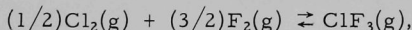
$\quad\quad \Delta H^o_{298} = -38 \text{ kcal/mole of } ClF_2;$

$\quad ClF_3(g) \rightleftarrows ClF(g) + F_2(g),$
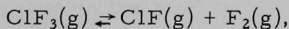
$\quad\quad \Delta H^o_{298} = -13 \text{ kcal/mole of } ClF.$

At lower temperatures (~300°C), formation of ClF_3 is faster than its decomposition and at higher temperatures, the decomposition is faster than its formation.

DeWitt[15] surveyed the physicochemical properties of UF_6. The sublimation point of UF_6 is 56.5°C at 1 atm. The formation of intermediate fluorides due to the reaction of UF_6 with UF_4 and their disproportionation was presented by Labaton.[16]

In the current bench-scale process development work, the UF_6, the main product of fluorination, is collected in cold traps maintained at -78.5°C by a dry ice-trichloroethylene bath. At the end of fluorination, the hexafluoride is hydrolyzed with dilute nitric acid and the solution is analyzed for uranium. The hydrolysis is a highly exothermic reaction, and the heat of reaction of solid UF_6 with liquid H_2O was reported by Popov et al.,[17] as follows:

$$UF_6(s) + xH_2O(1) = UO_2 F_2(sol.) + 4HF(aq.);$$
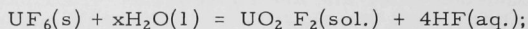
$$\Delta H°_{305} \text{ when } (x = 1600) = -50 \text{ kcal/mole.}$$

B. Earlier Process Development Studies

1. Studies of Complete Reaction Cycles. The fluid-bed volatility process involves volatilization of zirconium as its tetrachloride and retention of uranium as chlorides, and subsequent recovery of uranium as the volatile hexafluoride. Three contributions[18,19,20] studied the entire reaction cycle. Some of the individual process steps were studied in connection with the development of other processes.

An exploratory study of the hydrochlorination-fluorination reaction cycle was conducted in a $1\frac{1}{2}$-in.-diam. fluid-bed reactor at Brookhaven National Laboratory by Reilly et al.[18] The feasibility of the process was reported. Of the various materials tried in fluid beds, granular alumina (Alundum, manufactured by Norton Company) was found to be inert and satisfactory. Uranium recoveries ranged from 93 to 99% of the charge. Helium was used as the inert fluidizing gas. Use of packed-bed filters for retention of particulate uranium chlorides during hydrochlorination was reported. In addition to the studies in the $1\frac{1}{2}$-in.-diam. fluid-bed reactor, a few exploratory experiments were conducted on the hydrochlorination of multiplate fuel element subassemblies in a pilot plant.[21] Satisfactory hydrochlorination rates (~2 kg/hr) were achieved. This study facilitated the choice of equipment in the current work.

Similar attempts at developing the hydrochlorination-fluorination reaction cycle were made in laboratory studies at ANL by Johnson et al.[19] The hydrochlorination and fluorination reactions were conducted in a packed bed of alumina. After the hydrochlorination, the alumina bed was removed, mixed in a dry box, returned to the reactor, and then fluorinated. The concentration of uranium retained by alumina was low, ranging from 0.007 to 0.043 w/o. These results indicated high recovery of uranium could be expected.

Simultaneously with the research work at ANL, process-development work on a hydrochlorination-fluorination reaction cycle in a fluid bed was being carried out in France for recovering uranium from scrap uranium-Zircaloy-2 alloy. The results of these development studies with normal

uranium-Zircaloy-2 alloy using (1) a tube furnace, (2) a bench-scale fluid-bed reactor (using 100 to 300 g of fuel), (3) a pilot plant (1- to 3-kg fuel charges), and (4) a semicommercial plant (10- to 30-kg fuel charges) were reviewed by Faugeras.[20] The semicommercial plant had a 7.9-in.-diam. fluid-bed reactor. The alumina in the fluid bed was static during fluorination except for periodic fluidization. Residual uranium content of the alumina was ~200 ppm. The uranium loss during hydrochlorination was 0.1% of the uranium in the charge.

The effects of process operating conditions on uranium re-coveries have not been studied intensively. Until the present study was made, no data were available on the distributions of the fission products and the minor elements of Zircaloy-2 (most commonly used uranium-zirconium alloy); nor were data available on the possible decontamination factor, defined as the ratio of initial activity in the spent fuel to the final activity in the recovered fuel.

2. Studies of Individual Process Steps. Hydrochlorination, alone, of the uranium-Zircaloy-2 alloy was investigated while developing the Zircex[22,23] process (a head-end process for solid fuels). In the Zircex process, uranium-Zircaloy-2 alloy was reacted with HCl, and the uranium chloride residues were then subjected to aqueous dissolution for recovery of uranium by solvent extraction.

A hydrofluorination (treatment with HF) step can be incor-porated before the fluorination step in the fluid-bed fluoride volatility process to eliminate the chlorides associated with the uranium and other bed constituents; this results in UF_4 and prevents the formation of inter-halogen compounds. Literature on the fluorination of UF_4 was reviewed by Smiley.[24]

Recovery of UF_6 by cold-trapping methods has been studied extensively.[25,26] Chemical traps for UF_6, viz., NaF traps[27,28] and a bed of UF_4 fluidized by air,[29] were also subjects of extensive investigation.

Use of high-temperature packed-bed filters for retention of particulate solids in blast furnace gases was reported by Thring and Strauss.[30] The collection efficiency increased significantly with the inlet concentration of the solids and to a much smaller extent with mass flow rate of gas. The mechanism of filtration of particulate solids by packed-bed filters is not well established. Consequently the data were empirically analyzed.

III. EQUIPMENT AND PROCEDURE

A. Equipment

The equipment includes a $1\frac{1}{2}$-in.-diam. reactor assembly, a gas feed system, and auxiliaries for handling the reaction products and off-gases.

Figure 2

FLUID-BED REACTOR AND
PACKED-BED FILTER SECTIONS
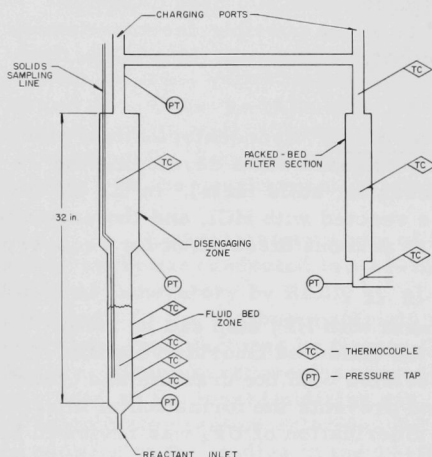
1. Fluid-bed Reactor and Packed-bed Filter Sections. The reactor assembly (see Figure 2) consists of the fluid-bed reactor and the packed-bed filter. The reactor is made up of the following three separate sections joined by flanges: 1) a bottom section, consisting of an inverted 60° cone with a single 1/4-in. IPS connection at the apex, which serves as both the gas inlet and the solids (bed) drainage point; 2) the fluid-bed section, a 14-in. length of 1.5-in. IPS pipe, heated by three 1000-Watt external electrical heaters and wrapped, also, with cooling coils; and 3) the top or disengaging section, a 14-in. length of 3.0-in. IPS pipe wrapped with four 1000-Watt heaters. The lower end of the disengaging section is necked down to mate with the fluid-bed section. The packed-bed filter, a 14-in. long section of 1.5-in. IPS pipe containing a packed bed of granular solids as the filter media, is connected to the reactor by a horizontal 1-in. IPS pipe; the ends of the connecting pipe have tee connections that provide openings for use as charging ports.

Thermocouples are affixed at several places on the outer surface of the reactor assembly and, also, are located internally (in wells) in the separate sections so that temperatures in the gas phase as well as in the beds can be monitored. The schematic outline of the reactor assembly shows the relative locations of important thermocouples, several of which are brought in through the top flanges. Pressure taps are provided to obtain differential pressure (Δp) measurements across both the fluid bed and the packed-bed filter. Sampling of the fluid bed during or after a particular operation is effected by means of a 1/8-in.-ID line which extends the length of the reactor to within 2 in. of the bottom. The entire assembly is wrapped with 2-in.-thick high-temperature insulation.

The cooling system for the main reactor section is shown schematically in Figure 3. Cooling is achieved by feeding a controlled air-water mixture to the stainless-steel cooling coil (1/4-in. OD, 15 ft long) wound on the reactor. The water is fed from a reservoir (Pyrex glass, $2\frac{1}{2}$-in. ID, 12 in. long) into the cooling air stream through a manually-preset needle valve. The air is fed separately through an air-operated proportional diaphragm-control valve. The flow of air and water are regulated separately by a single proportional output from a temperature controller, upon demand from a thermocouple on the reactor wall. To prevent erratic cooling from possible water slugs, a manual bypass system on the control valve provides a continuous air bleed.
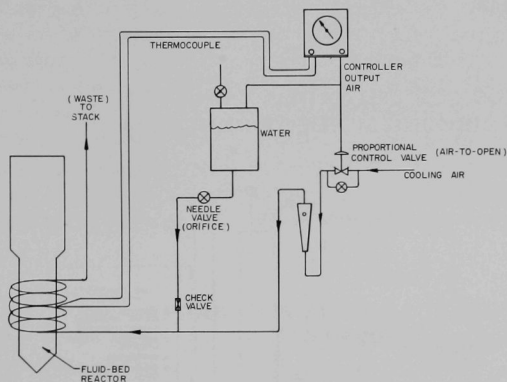
Figure 3

PROPORTIONAL AIR-WATER
COOLING SYSTEM

2. Gas Feed System. The gases used during the reaction cycle are HCl, HF, fluorine, and nitrogen (for dilution, purges, and fluidizing purposes). The reactants are fed from supply cylinders and manifolded into a single feed system. Nitrogen was provided from a liquid nitrogen supply.

The HCl and fluorine feed systems are similar and consist of 1) two single-stage pressure regulators in series, 2) a manual control valve, 3) a Teflon-packed Pyrex glass rotameter with a stainless-steel float, and 4) a thermal flow meter.[31]

The HF is vaporized from a heated cylinder and is metered through a Kel-F rotameter with a nickel float. A pressure controller regulates the heat input to the cylinder. To prevent condensation of the HF in the distribution system, the entire system is heated by external tracing with asbestos-wrapped Nichrome heating wire.

The feed gas stream is preheated as it passes through a 6-ft-long, 3/8-in.-OD nickel tube, connected to the reactor inlet. The heat

is provided by a 1000-Watt Nichrome wire heater, wound on the tube. Total flow of the feed gas stream is recorded by using an "orifice-d/p cell system,"* the orifice plate being located upstream of the preheater.

3. Auxiliary Equipment for the Hydrochlorination Step. During the hydrochlorination step, the following three auxiliary items, all made of standard 4-in.-diam. Pyrex glass sections, are used: 1) a HCl saturator during some runs, 2) a $ZrCl_4$ condenser, and 3) a HCl disposal tower (Figure 4). The saturator for the inlet HCl gas is 33 in. high, packed to a height of 12 in. with 1-in. ceramic Berl saddles, and filled with concentrated hydrochloric acid to a height of about 18 in. With this unit, the recycle of HCl containing a fixed quantity of water (the equilibrium moisture content) is simulated.

Figure 4

APPARATUS FOR CHLORINATION OF
URANIUM-ZIRCONIUM ALLOY FUELS
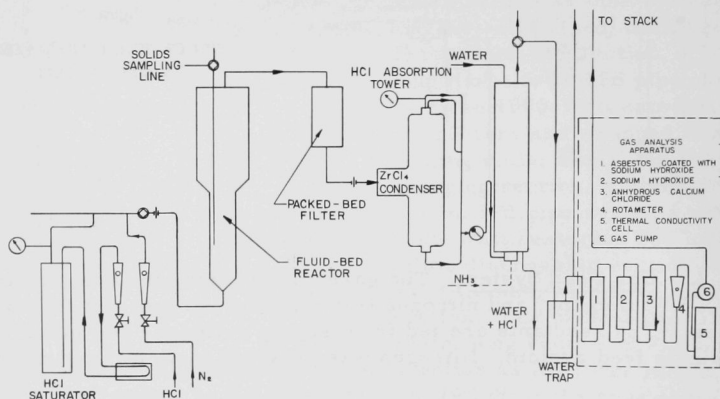
The $ZrCl_4$ condenser is an ambient-air-cooled glass tee-section mounted vertically and fitted with metal cover flanges for making the necessary inlet and outlet pipe connections. The branch end of the tee is connected with a 1-in. union to the exit of the packed-bed filter. The ends of the run of the tee are packed with glass wool to retain entrained $ZrCl_4$ particulate solids. Three 3/8-in.-OD outlet tubes, two at the top and one at the bottom, are provided on the condenser for the exiting HCl off-gas. These outlet tubes are manifolded to a line that leads to the HCl disposal tower, a 4-ft-high unit packed to a height of 28 in. with 1/2-in. ceramic Raschig rings with water sprayed from the top. An inverted U-tube and ball-check valve are used between the condenser and

*Manufactured by Foxboro Company, Foxboro, Massachusetts.

the scrubber to prevent backup of aqueous scrub solution. The off-gas from the ZrCl$_4$ condenser enters at the bottom of the scrubber through an annulus section, the central tube serving as an inlet for ammonia if neutralization is needed. The off-gas exits at the top of the tower through a de-entrainment section (a $3\frac{1}{2}$-in.-diam., 6-in.-high bottle) for removal of entrained water. The main outlet from this section then leads to an exhaust duct; a second outlet provides sample gas for off-gas analysis (see par. 5 below). An outlet for the scrub solution is provided at the bottom of the tower.

4. Auxiliary Equipment for the Fluorination Step. Important items of equipment for the fluorination step include the UF$_6$ collection traps and a fluorine disposal tower (see Figure 5). The UF$_6$ trap system consists of five coils connected in series, each coil being wound of a 5-ft-long tube. The first two coils are made of 1/2-in.-OD copper tubing; the others are constructed of 3/8-in.-OD nickel tubing. The first coil is immersed in an ice bath; the second, third, and fifth are immersed in a dry ice-trichloroethylene bath (-78.5°C). The fourth coil is kept at room temperature to allow revaporization of UF$_6$ mist ("snow") formed in the first three traps as a result of too-rapid cooling of the UF$_6$ vapors; final trapping of UF$_6$ is effected in the last trap.

Figure 5

APPARATUS FOR RECOVERY OF URANIUM
BY FLUORINATION
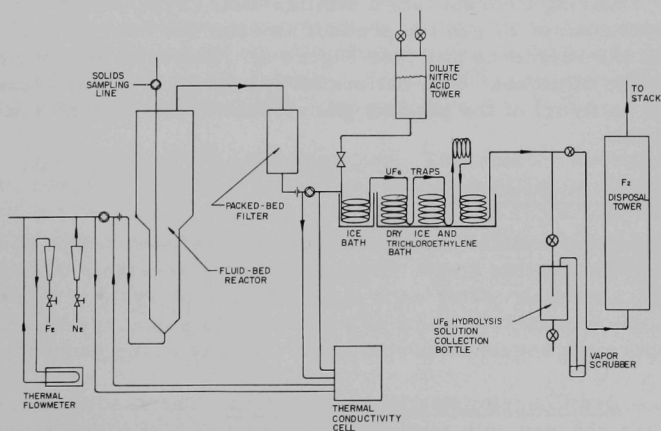
Fluorine is disposed of by reaction with activated alumina. The fluorine disposal tower (3-in. ID, 36-in. long, ambient-air-cooled) is made of nickel and contains 1/4-in.-diam. activated alumina spheres. The

consumption of alumina is detected by following the temperature of the reaction zone along the column axis. The off-gas from this unit passes directly to the stack.

5. Thermal Conductivity Cells for Off-gas Analysis. Thermal conductivity cells (hereafter referred to as TCC's) are used during the entire reaction sequence - hydrochlorination, hydrofluorination, and fluorination - to follow the progress of the reactions. Nickel filament cells are satisfactory for all three steps; however, a glass-bead thermistor type was used initially during hydrochlorination and was retained for convenience. The construction and application of the TCC's are discussed in detail in the appendix.

For following the progress of the hydrochlorination and hydrofluorination steps, the concentration of hydrogen in the off-gas is measured by a glass-bead TCC. The off-gas sample passes through a purification system consisting of a series of three 2-in.-diam., 12-in.-high, brass tubes (see Figure 4), containing granular Ascarite,* sodium hydroxide pellets, and anhydrous calcium chloride, respectively, and a rotameter before being introduced into the TCC. The gas sample is pumped out from the TCC to the atmosphere by a Gast oilless compressor with a 1/40-hp motor. The TCC is an "on-stream" ambient-temperature-controlled type, made of stainless steel (Type 9680).** Nitrogen is used as the reference gas.

During fluorination, a similar TCC (Type 9454)** measures the concentration of UF_6 in the product stream, the inlet fluorine stream serving as the reference gas (see Figure 5). The detector body and the filaments are of nickel. Two calibrated 1/2-in. plug valves channel a part (0.2 to 2.0 cu ft/hr) of the product gas stream to the thermal conductivity detection unit.

B. Experimental Procedure

The experimental procedure includes prefluorination, hydrochlorination, and fluorination steps. Regulation of the reactants during each step is by manual control. After each step, the reactor system is purged with nitrogen; the appropriate items of auxiliary equipment are then installed, and the operating sequence is continued. Details of the procedure follow.

1. Bed Charging and Prefluorination. The reactor and filter sections are charged with specified quantities of high-fired granular alumina as bed materials. Minimum fluidization velocities were determined for the

---

*Trade-name for asbestos coated with sodium hydroxide, used by Arthur H. Thomas Company, Philadelphia, Pa., U.S.A.

**Manufactured by Gow-Mac Company, New Jersey, U.S.A.

various bed materials with nitrogen, HCl, HF, and fluorine since these could not be accurately calculated. The entire assembly is then prefluorinated at 500°C for 2 hr with an equimolar mixture of fluorine and nitrogen.

2. Hydrochlorination. The hydrochlorination step is the longest operation in the cycle and begins with the charging of the fuel alloy sub-assemblies (alloy chips were also used) to the fluid-bed reactor. The fuel elements are lowered onto the alumina bed while the bed is in a static condition. Upon fluidization of the bed, the elements submerge into position for reaction. All the required auxiliary equipment, such as the $ZrCl_4$ condenser, is installed. Fluidization is started with nitrogen, and the reactor and filter are heated. When the system is at the prescribed temperature, nitrogen flow is reduced and HCl flow gradually increased until the desired HCl concentration is reached. To ensure completion of reaction, feeding of HCl is continued for about a half-hour after the TCC has indicated that hydrogen production has ceased.

3. Hydrofluorination. For the hydrofluorination step, the $ZrCl_4$ condenser is replaced by a 3/8-in.-OD nickel line which connects the packed-bed filter directly to the scrub tower. Ammonia is fed to the scrub tower to neutralize the excess HF.

4. Fluorination. After hydrofluorination and after all the necessary auxiliary equipment for the fluorination step is connected, the reactor bed is again fluidized with nitrogen. Fluorine is carefully intro-duced and maintained at a relatively low concentration for a given time-temperature cycle. Fluorine concentration is then increased to a high value. The fluorination is terminated after a given cycle has been com-pleted. Final conditions are a relatively high (~90%) concentration of fluorine and a relatively high (500°C) temperature.

5. Hydrolysis of UF_6 and Sampling. The reactor assembly is purged with nitrogen, isolated, and, to prevent in-leakage of air, main-tained under a pressure of 10 psig. The UF_6 product traps are isolated by turning off appropriate valves and then immersed in an ice bath. The UF_6 is dissolved in dilute nitric acid. Dilute nitric (10 w/o) acid, at a rate equivalent to approximately 25 ml per gram of UF_6, is passed through the traps with nitrogen. The hydrolysis solution is collected in a receiver; the exit gases are scrubbed with sodium hydroxide solution before being vented. The traps are washed twice more with similar quantities of dilute nitric acid to ensure complete removal of the uranium. The solution is analyzed for uranium and impurities.

Samples of the beds and various streams were taken to de-termine the distribution and concentration of uranium at various stages of the process. Fluid-bed samples were taken at any desired time during the entire reaction sequence. After hydrochlorination, samples of the condensed $ZrCl_4$ were obtained after in situ dissolution of the condensate

in 20 w/o hydrochloric acid (approximately 4 ml of acid per gram of $ZrCl_4$). The exit liquid stream from the scrub tower was sampled every half-hour during scrubber operation. The activated alumina in the fluorine disposal tower was also sampled.

IV. HYDROCHLORINATION FOR SEPARATION OF ZIRCONIUM

Hydrochlorination of the alloy is carried out to separate the bulk material in the fuel, the cladding and the alloying agent (zirconium), from the uranium, and to provide the uranium in a form amenable to recovery by fluorination. Separation is achieved by carrying out the reaction at temperatures above the sublimation point of $ZrCl_4$ (331°C at 1 atm). The uranium is converted to solid chlorides. Uranium and other particulate solids entrained in the HCl gas stream are retained in the system by a packed bed of alumina which serves as a high-temperature filter. The progress of the hydrochlorination reaction is followed by continuously measuring the concentration of hydrogen in the off-gas with an in-line thermal conductivity cell. During this investigation, 40 experiments were completed. The experimental data are summarized in the appendix.

A. Scope of Hydrochlorination Conditions

The range of hydrochlorination conditions studied in the development of this process is shown in Table I.

Table I

RANGES OF HYDROCHLORINATION OPERATING VARIABLES INVESTIGATED

Total number of experiments: 40

Fuel Charges
Weight: 160 to 400 g of alloy (1 to 3 charges per run), 4.8 to 13.7 g of simulated fission products

Concentration of uranium: 1 to 5 w/o

Shapes: Chips, $\frac{1}{8}$- to $\frac{1}{4}$-in. size, and miniature fuel element subassemblies

Alumina Charges
Fluid bed: High-fired aluminas (sintered and fused types) 320 to 550 g, 30 to 120 mesh sizes

Packed-bed filter: Sintered and fused aluminas
0 to 2850 g
0 to 12 in. deep
Upward and downward gas flow

Temperature
Fluid bed: 330 to 550°C
Fluid-bed reactor wall: 330 to 550°C
Packed-bed filter: 330 to 550°C

Reactant Conditions
HCl concentration: 0 to 90 v/o

Quantity of HCl: 2.5 to 25 stoichiometric amounts needed to convert zirconium to its tetrachloride

Moisture content of HCl: 0 to 1100 ppm

Concentration of hydrogen in HCl: 20 v/o

Chlorinating agents other than HCl: Mixture of hydrogen and chlorine; HCl followed by $COCl_2$; mixture of HCl and $COCl_2$

1. <u>Fuel Charge</u>. Fuel charges in the form of chips ($\frac{1}{8}$- to $\frac{1}{4}$-in. size) and miniature multiplate subassemblies were processed. The chips (2.7 to 5.2 w/o uranium) were considered as representative of scrap alloy, while multiplate subassemblies were used to more nearly simulate actual fuel elements. Each subassembly, weighing 160 to 200 g, consisted of three normal uranium-Zircaloy-2 alloy plate sections clad with Zircaloy-2 and inert-arc-spot welded[32] together. One subassembly was constructed with an arbitrary plate spacing of 0.125 in., while the others were made with plate spacing of 0.069 in. similar to that used for the fuel elements in the Shippingport Pressurized Water Reactor.[33] The overall uranium concentration in the subassemblies was about 1 to 2 w/o.

2. <u>Alumina Charges</u>. High-fired alumina grain of two different qualities (sintered and fused) was used as inert bed material in both the fluid bed and the packed-bed filter. The mesh size of alumina charged to the fluid bed was varied over the range of 30 to 120 mesh. The mesh size of alumina in the packed-bed filter was varied from -14 +20 mesh to -80 +200 mesh, and -14 +20 mesh was found satisfactory. The bed depth of the filter was varied from 0 to 12 in. to evaluate its effect on uranium loss. Tests were performed with the packed-bed filter to compare the effectiveness of filtration of gas with the flow in either an upward or downward direction. A down-flow system appeared to be more suitable for application to the process.

3. <u>Hydrochlorination Temperature</u>. The temperatures of the fluid bed and the reactor wall were varied in the range of 350 to 550°C. It was observed that reactor walls have to be maintained below 400°C to reduce corrosion to a tolerable level, while the temperature of the fluid bed may be allowed to rise as high as 500°C commensurate with the upper limits for service with metal equipment.

4. <u>Reactant Conditions</u>. To determine processing conditions that would result in high reaction rates and high HCl utilization, exploratory tests were performed in which the HCl concentration was varied from 0 to 90 v/o. The effect of the amount of HCl fed to the reactor was studied as the quantity was varied tenfold from 2.5 to 25 times the stoichiometric amount needed to convert zirconium to its tetrachloride. In the conceptual operation of the process (see flowsheet, Figure 13), the off-gas from the fluid-bed pyrohydrolysis reactor (for the disposal of $ZrCl_4$ as ZrO_2) may be fed to a condenser at 21°C; part of the off-gas would condense as aqueous HCl, and the exit gas stream containing an equilibrium moisture content of 1100 ppm may then be recycled. The HCl recycle was simulated in several runs by feeding moist HCl. In other experiments of an exploratory nature, hydrogen was fed along with HCl. Two alternative chlorinating agents, (1) a mixture of hydrogen and chlorine, and (2) phosgene ($COCl_2$), were used.

B. Uranium Distribution during Hydrochlorination

During hydrochlorination, the uranium contained in the fuel charge is converted to both particulate and vapor forms of chlorides. Both uranium and chloride contents of the fluid bed were determined in an attempt to learn the chemical form of the particulate uranium present. Samples taken from the fluid bed showed a chloride-to-uranium mole ratio of 3.0 after hydrochlorination, indicating that uranium was present principally as the trichloride, and very little, if any, additional chloride was associated with either the alumina grain or other residual materials (zirconium and impurities).

After the alloy has been reacted, the uranium distribution in the system is found to be about as follows: the major part, as particulate uranium chloride, is retained in the fluid bed; part of it (found to be about 20%) is entrained by the gas stream leaving the fluid bed and is collected by the packed-bed filter; and a very small fraction is lost in the form of uranium chloride particulate (subfilterable) and/or vapor in the exit gas stream from the packed-bed filter. The main concern at this point in the process is the fraction lost. As the work progressed, these losses were reduced by an order of magnitude from 0.3% of the uranium in the initial charge to rather insignificant average values of 0.04%. A particular series of ten experiments, in which the quantity of uranium in the alloy charge ranged from 4.0 to 36.1 g, gave losses ranging from a maximum of 0.1% to a minimum of 0.02%.

1. Overall Effects of Hydrochlorination Conditions on Uranium Loss. Uranium losses during hydrochlorination are comprised of both volatile and particulate forms of chlorides. Phenomena associated with losses include a) production of filterable and subfilterable grades of particulate chlorides, and b) volatilization, or the formation of a volatile chloride species. Phenomena associated with uranium retention include a) filteration of the off-gas by the packed-bed filter, and b) condensation of the volatile species. All of these phenomena are affected by the reaction conditions; i.e., the reaction conditions affect the quantity and quality (size, form) of the particulate and volatile forms produced.

A statistical study [stepwise multiple regression analysis[34]] was performed at the end of the current investigation to establish the relative effects of all the process operating variables of the hydrochlorination step on uranium losses. The results of this study (data from 27 experiments) in terms of the above phenomena suggest that the overall process of retaining uranium in the system may not be one of filtration of particulate material, alone, but rather, may include both the production and filtration of the particulate species and the production and condensation of the volatile species. The effects of the hydrochlorination variables on uranium losses in terms of these phenomena are given below in order of

the apparent decreasing importance of the variable (i.e., the first variable is the most significant, and the last one is the least significant). Losses were found to be lower when:

1. The filter-bed depth was increased from 0 to 12 in.; deeper beds gave better filtration of particulate species and allowed greater condensation of volatile species.

2. The average partial pressure of HCl was lowered (in the range of 0.88 to 0.17 atm); the formation of volatile species was probably decreased.

3. The average particle size of alumina in the packed-bed filter was decreased from ~1.4 (nominal 14 mesh) to 0.125 mm (nominal 120 mesh); smaller particles gave better filtration and allowed greater condensation. In some cases, the filter section contained no bed; retention by the walls was observed.

4. The temperature attained by the gas stream between the fluid bed and the outlet of the filter bed was lowered from 400 to 320°C; greater condensation of the volatile species was effected.

5. The average particle size of alumina in the fluid bed was decreased from 0.42 (nominal 40 mesh) to 0.125 mm (nominal 120 mesh); possibly a combination of all four effects, viz., production and filtration of particulate species, formation and condensation of volatile species, was in operation.

6. The average hydrochlorination rate of uranium was decreased from 0.268 to 0.016 kg/(hr) (sq ft of fluid-bed reactor cross section); the relative amounts and the physical characteristics of uranium chlorides formed were affected.

In addition to the above, the feeding of hydrogen along with HCl (simulating recycle) was expected[2] to reduce the more volatile UCl_4 to a filterable particulate form, UCl_3, thereby resulting in lower uranium losses. The uranium losses were low in both the presence and absence of hydrogen, and there was no effect of hydrogen concentration on uranium loss.

2. _Temperature Effect._ An interesting correlation was found to exist between the temperatures in the reactor assembly and the uranium losses through the packed-bed filter. This correlation showed effectively that a vaporization, or conversely a condensation, phenomenon was involved,

both of these being temperature-dependent. Experimental data on the average rate of uranium loss through the packed-bed filter were plotted as a function of the lowest temperature attained by the gas stream between the fluid bed and the distal end of the packed-bed filter. A semilog dependency was found (see Figure 6), indicating loss by vaporization as the probable mechanism, the most likely species being UCl_4. Uranium trichloride has negligible vapor pressures [e.g., 5×10^{-10} mm Hg at 350°C by extrapolation[2]] in this temperature range of 320 to 390°C. Calculations based on reported values[35] for the vapor pressure of UCl_4 (e.g., 3.7×10^{-4} mm at 350°C) indicate the exit gas was about 50% saturated under most of the experimental conditions. The principal conclusion to be drawn from this information is that the packed-bed filter should be operated at as low a temperature as possible to minimize uranium loss.

Figure 6

URANIUM LOSS DURING HYDROCHLORINATION OF URANIUM-ZIRCONIUM ALLOY FUELS

Average rate of uranium loss versus 1/T where T (°K) is measured in the reactor assembly and is the lowest temperature between the fluid bed and the outlet of the packed-bed filter.

O RUNS WITH THE PACKED-BED FILTER CONNECTED IN SERIES WITH THE FLUID BED.
X RUNS WITH AN EMPTY, 1-1/2 in. "SETTLING" CHAMBER INSTALLED BETWEEN THE FLUID-BED REACTOR AND THE PACKED-BED FILTER.
Δ PACKED-BED FILTER SECTION IN SERIES WITH THE FLUID BED BUT CONTAINED NO BED.
□ HYDROGEN INTRODUCED ALONG WITH THE FEED; PACKED-BED FILTER CONNECTED IN SERIES WITH THE FLUID BED.

(NUMBERS REFER TO SPECIFIC RUNS)

CALCULATED LOSS IF THE EXIT GAS STREAM IS SATURATED WITH UCl_4

108-6885 Rev.

In summary, results showed that a packed-bed filter containing a 6-in.-deep bed of -14 +20 mesh alumina maintained at the lowest possible temperature (~330°C) gave the lowest uranium losses (~0.04%).

C. Fuel Reaction Rates and Hydrogen Chloride Utilization Efficiency

Several phenomena associated with the hydrochlorination step were of interest and were investigated in single- and multiple-alloy-charge experiments. These were (1) the behavior of the fuel, (2) temperature phenomena, and (3) hydrochlorination rate and HCl utilization efficiency. For simplicity, the hydrochlorination rate was defined as the mass of fuel reacted per unit time. The HCl utilization efficiency, E, was defined as

$$E = \frac{HCl \ reacted}{HCl \ input} \times 100.$$

The reaction rate and the HCl utilization efficiency were both calculated from data on the amount of hydrogen evolved, assuming the reaction

$$Zr + 4HCl \rightarrow ZrCl_4 + 2H_2.$$
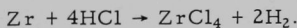
This calculation disregards the presence of the other elements in the Zircaloy charge.

    1.   <u>Behavior of Fuel</u>. In the conceptual process, multiplate sub-assemblies or clusters of assemblies [usually 6 to 8 ft long, either $2\frac{1}{2}$ or 6 in. square[33]], will be charged to the fluid-bed reactor for hydrochlorination. The HCl will be fed from the bottom of the fluid bed, and the behavior of the fuel during hydrochlorination is of interest. Inspection of a partially hydrochlorinated multiplate fuel element subassembly showed that (1) the subassembly was reacted more at the bottom (see Figure 7b),

Figure 7

BEHAVIOR OF A MINIATURE URANIUM-ZIRCONIUM ALLOY FUEL ELEMENT
SUBASSEMBLY DURING HYDROCHLORINATION

a) Original Element - Side
View - Initial Weight:
160 g

b) Partially Hydrochlorinated
Element - Side View -
Weight: 89 g

c) Original Element - Bottom View Showing
Relative Size of Bed Material (Alumina)
to Plate Spacing

d) Partially Hydrochlorinated Element -
Bottom View

108-5827 Rev.

Scale in Inches
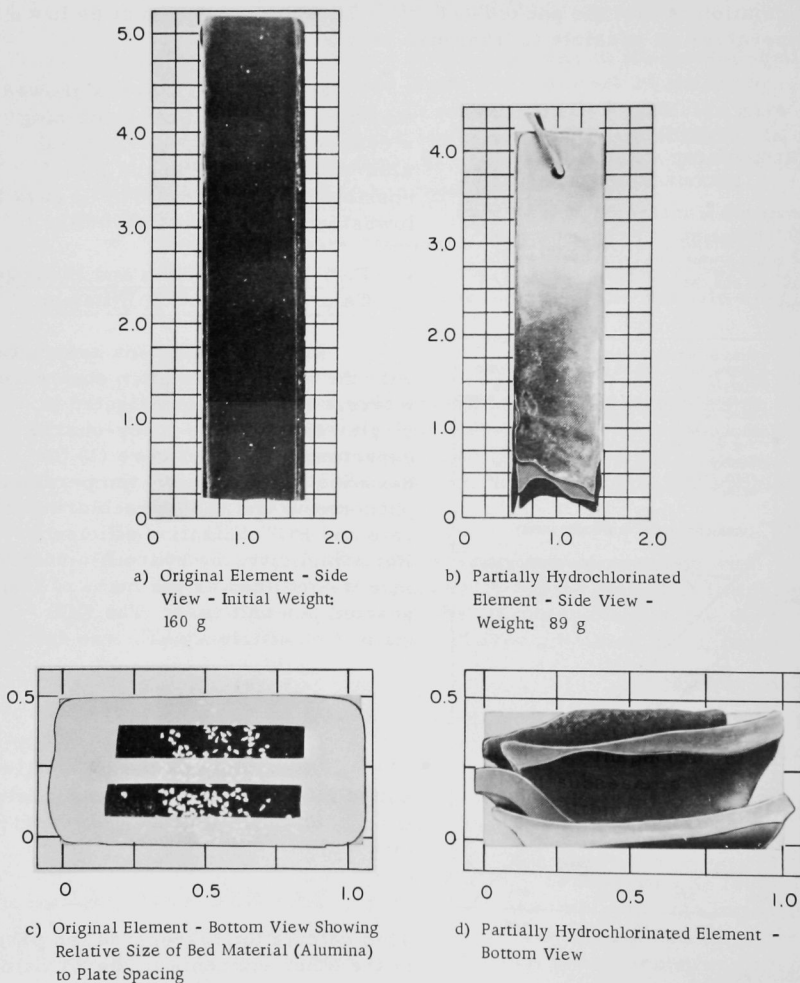
the region which was first contacted by the inlet gases; (2) the extent of hydrochlorination of the plates decreased gradually with increase in height in the direction of gas flow, the tops of the plates appearing completely un-reacted (possibly due to depletion of HCl in the gas stream); and (3) the bottom ends of all three plates were extensively but nonuniformly reacted (see Figure 7d), indicating high localized reaction rates and the possible existence of localized hot spots on the fuel element. A side view of the original element is shown in Figure 7a. The sizes of plate spacing and the granular alumina in the fluid bed are compared in Figure 7c.

The gradual decrease in the extent of hydrochlorination of the fuel element subassembly from the bottom to the top indicates that (a) the HCl fed at the bottom of the fluidized bed may be more completely utilized with longer elements than with shorter ones, and (b) multiple HCl feed inlets may result in higher hydrochlorination rates, but may lower the efficiency of utilization of HCl in comparison to a single HCl inlet at the bottom of the fluid bed.

2.   Temperature Phenomena during Hydrochlorination. Experi-ments were performed to investigate relative temperature effects during hydrochlorination. An atypical experiment was conducted under severe hydrochlorination conditions to determine whether this reaction could get out of control and fuel temperatures would exceed the melting points of the uranium chlorides that are produced. The fuel temperature was measured with a thermocouple affixed to the multiplate subassembly. The inlet HCl, normally diluted with nitrogen, was fed undiluted in this case. The temperatures of the fuel, the fluid bed, and the reactor wall were continu-ously recorded for the entire period (5.3 hr) of hydrochlorination and are plotted in Figure 8.
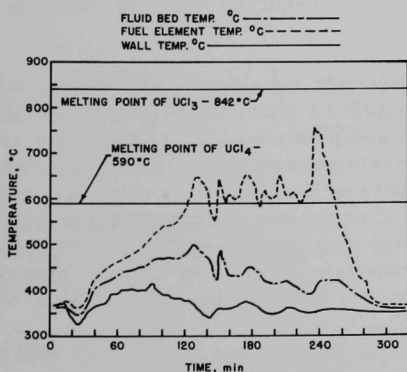
Figure 8

TEMPERATURE PHENOMENA DURING HYDROCHLORINATION

Fuel Charge: Uranium-Zircaloy-2
Alloy Fuel Element Subassembly

108-7370

In spite of the use of extreme hydrochlorination conditions, the reaction remained under control throughout the experiment. Fuel temperatures as high as 750°C were recorded, but this level is well below the melting point of UCl_3 (840°C), the major uranium chloride formed during hydrochlorination. During a 2-hr intermediate period, the fuel temperatures did exceed the melting point of the other uranium chloride that may form (UCl_4, mp 590°C). During this period of high fuel temperatures, the temperatures of the fluid bed and the wall were relatively low, averaging about 430 and 360°C, respectively. The highest fuel temperatures were sustained after the major amount ($>50\%$) of the subassembly was reacted, whereas the fluid-bed temperature peak (500°C) was attained earlier when the major amount of the subassembly was still present. The temperature of the reactor wall reached a maximum of 415°C and averaged 370°C for the entire experiment, indicating that excellent heat transfer was occurring in the system. Under these conditions, the hydrochlorination rates reached a maximum of 100 g/hr of fuel, which corresponds to about 700 mg/(sq cm)(hr).

In normal runs, lower ($< 75\%$) HCl concentrations were used and the fuel temperatures were considerably lower than those noted above even though similar overall reaction rates were achieved. The temperatures of the fuel and the fluid bed were allowed to rise to achieve the desired overall reaction rates while maintaining the temperature of the reactor walls below 380°C. Typical temperature ranges were 366 to 554°C for the fuel, and 366 to 446°C for the fluid bed.

3. Hydrochlorination Rate and HCl Utilization Efficiency. Similar HCl utilization efficiencies were achieved with both the multiplate subassemblies and the alloy chips. The overall HCl requirements were about 2.5 times the stoichiometric amount required to convert all the charge as zirconium to the tetrachloride.

With the multiplate fuel element subassemblies it was found that higher reaction rates, higher HCl utilization efficiencies, and lower alloy temperatures were achieved when mixed particle sizes of bed material (alumina) were used instead of relatively narrow sieve fractions. The improvements may be due to the quality of fluidization that is achieved, known to be better with mixed sizes of particles. Further, it was observed that the utilization efficiency increased with a decrease in the ratio of plate spacing-to-average particle diameter (from 12 to 4.7). Information on this relationship will be presented in a forthcoming report, ANL-6830.

The average hydrochlorination rates and the overall efficiencies of HCl utilization appeared to be independent of the moisture content of the HCl up to a level of 1100 ppm. Average rates of 28 and 27 g/hr were sustained for runs with 1100 and 35 ppm moisture in HCl. In general, when

moist HCl was used, the hydrochlorination proceeded without any erratic fluctuations in either the reaction rates or the temperatures of the fuel and the fluid bed, indicating that water vapor may reduce the instantaneous hydrochlorination rate and have a stabilizing influence on the hydrochlorination as a whole.

4. Multiple-batch Hydrochlorinations. The entire hydrochlorination period for a single charge of fuel may be divided into two parts, viz., a constant-rate period and a falling-rate period (see Figure 9). During the constant-rate period, the reaction in the fluidized bed is self-sustaining; i.e., the heat produced by the hydrochlorination is equal to the sum of the heat losses to the surroundings and the heat removed by the gas streams. External heating may not be needed to maintain the fluidized bed at temperature. Steady state may be attained with respect to the concentration and flow rate of gas streams. Efficiency of HCl utilization is constant. During the falling-rate period, the reaction in the fluidized bed is not self-sustaining; i.e., the temperature of the fluidized bed has to be maintained by stopping the flow of the coolant and/or by supplying heat from external heaters. Utilization of HCl decreases rapidly.

Figure 9
ALTERNATIVE SCHEMES FOR
MULTIPLE-BATCH
HYDROCHLORINATIONS
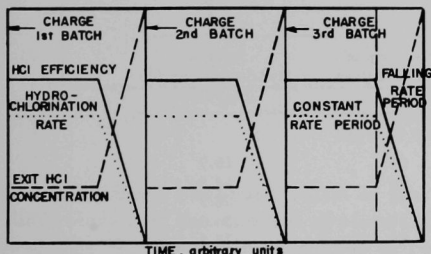
(a) COMPLETE HYDROCHLORINATION WITH EACH BATCH
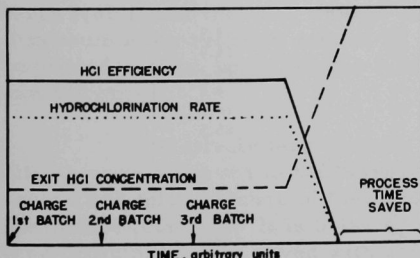
(b) IDEAL MULTIPLE-BATCH HYDROCHLORINATION

From the above observations it may be concluded that for optimum efficiency a fresh batch of fuel may be charged soon after the constant-rate period for the preceding batch has ended (see Figure 9). By performing most of the hydrochlorination during the constant-rate period, considerable saving in processing times may be achieved and the overall efficiency of HCl utilization can be greatly improved.

To test the concept of multiple batching, three batches of fuel chips ($\frac{1}{4}$- to $\frac{1}{8}$-in. size) were processed in succession. The first batch was partially hydrochlorinated, and then the second batch was charged. After partial hydrochlorination of the second batch and the residual fuel from the first batch, the third batch of fuel was charged. The progress of hydrochlorination was followed by the amount of hydrogen produced and was stopped when hydrogen could no longer be detected.

The values of the HCl utilization efficiency, the fuel reaction rate, and the inlet concentration of HCl for the entire period (21.3 hr) of hydrochlorination, are reported in Table II and are plotted in Figure 10.

Table II

HYDROCHLORINATION OF THREE BATCHES OF URANIUM-ZIRCALOY ALLOY FUEL

Fuel Charge: Three batches, 240 g each, 5.0 w/o uranium-Zircaloy-2 alloy chips ($\frac{1}{8}$- to $\frac{1}{4}$-in. size)

Reaction Bed: 320 g of alumina, -40 +60 mesh (Norton Co., Type RR Alundum)

Packed-bed Filter: 120 g of alumina, -40 +60 mesh (Norton Co., Type RR); 200 g of alumina, -14 +20 mesh (Norton Co., Type 38 Alundum)

Hydrochlorination
Temperature: 400 ± 25°C

Diluent Gas: Nitrogen

Volume Flow
Rate of Gas: 15 cfh (70°F, 1 atm)

Run Time (hr)	Inlet HCl Concentration (m/o)	Efficiency of HCl Utilization (%)	Rate of Hydrochlorination (g/hr)
0	First Batch of Fuel Charged		
0.33	6	65	15.9
0.66	7	74	14.3
1.0	15	75	36.1
2.0	17	69	33.4
3.0	17	69	33.4
4.0	95	7	18.0
4.03	Second Batch of Fuel Charged[a]		
4.36	7	60	14.9
4.69	7	60	14.9
5.03	8	58	14.3
6.03	3	30	4.2
7.03	6	60	14.9
8.03	8	73	26.5
8.19	Third Batch of Fuel Charged[b]		
8.52	5	70	10.6
8.85	5	74	11.1
9.19	8	30	8.5
10.19	8	70	17.0
11.19	11	63	23.3
12.19	15	80	33.4
13.19	25	51	41.9
14.19	26	56	38.7
15.19	22	41	29.7
16.19	36	32	38.7
17.19	85	9	20.7
18.19	85	12	49.5
19.19	95	5	12.2
20.19	95	3	7.4
21.0	95	< 0.4	0.8

[a]The second batch of fuel was charged after about 50% of the first charge had been reacted.

[b]The final batch of fuel was charged after about 37% of the first two charges had been reacted.

Figure 10

HYDROCHLORINATION OF THREE BATCHES
OF URANIUM-ZIRCALOY FUEL
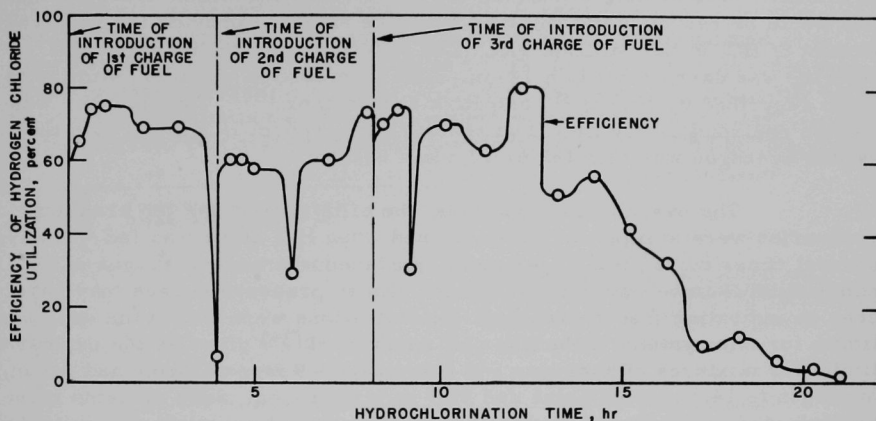
The maximum observed value of the efficiency was 80%. Because of the inefficiency of the coolant system (air was being used in an external $\frac{1}{4}$-in.-diam. coil) in removing the heat of reaction, it was necessary to limit the inlet HCl concentration to ~20 m/o during the portions of the run when a large fraction of the alloy charge was present. This HCl rate gave a maximum alloy reaction rate of 50 g/hr and an overall rate of 34 g/hr. An improved coolant (an air-water mixture) was provided for subsequent experiments.

Relatively long periods of operation under steady-state conditions were achieved in this experiment, but the time of charging the second and third batches of fuel was not optimum because of the manual operations (control). It is believed that considerable hydrochlorination time could have been saved with proper control of the system, and the multiple-batch concept warrants consideration in scale-up work.

D. Other Chlorinating Agents

During the development work, two alternative chlorinating agents were tested. These chlorinating agents were (1) a gas mixture of hydrogen and chlorine, and (2) phosgene ($COCl_2$); $COCl_2$ was used both admixed with HCl and separately following a period of HCl. The use of these was found to be of no particular advantage. However, results from tests in which these agents were evaluated are summarized and discussed here primarily to mention why these agents were considered unsatisfactory.

1. Gas Mixture of Hydrogen and Chlorine as a Chlorinating Agent.
An exploratory experiment was made to investigate the use of a mixture of
hydrogen and chlorine streams as a chlorinating agent. Nitrogen was used
as diluent. This system simulated the condition under which hydrogen and
HCl would be recycled and chlorine would be added to provide the required
amount of HCl in the reactant gas. The reaction between hydrogen and
chlorine was carried out in a $1\frac{1}{2}$-in.-diam. combustion chamber, similar to
those described by Maude[36] and Kirk and Othmer.[37] The chamber was
located upstream of the fluid-bed reactor; the product HCl along with the
excess hydrogen was then fed to the main reactor.

The overall reaction rates, the efficiencies, and the uranium
recoveries were similar to those obtained when HCl alone was fed. However,
several times during this experiment spontaneous pressure surges in the
combustion chamber were encountered. These pressure surges may have
been an indication that the reactant concentrations were within the explosion
limits for this system. Induction coil spark work[38] gives as the explosive
limits for mixtures of hydrogen and chlorine, 91.9 m/o chlorine and 8.1 m/o
hydrogen to 14.3 m/o chlorine and 85.7 m/o hydrogen. Such systems must
be evaluated carefully before they can be considered practical and reliable.

2. Phosgene as a Chlorinating Agent. Phosgene was evaluated as
a chlorinating agent during hydrochlorination to promote elimination of the
residual amounts of zirconium (possibly present as oxide). In earlier
work, residual zirconium was suspected of being associated with the
retention of uranium by alumina.

Elimination of zirconium by phosgene was achieved, zirconium
contents of the fluid bed being reduced from 0.12 to 0.02 w/o in 1-hr
periods at either 350 or 400°C; however, no direct effect of zirconium (in
concentrations up to 2 w/o) on uranium retention has been observed in this
study (see fluorination results, Sec. VI below).

V. HYDROFLUORINATION FOR REMOVING CHLORIDES

Elimination of the chloride associated with the uranium and other
bed constituents before the introduction of fluorine avoids the formation
of interhalogen compounds and is considered to be of possible process
interest. This can be readily achieved by a hydrofluorination step as
discussed below.

Hydrofluorination at 400°C of a fluidized bed containing the
products of a HCl-COCl$_2$ run reduced the concentration of chloride from

0.47 to 0.015 w/o in about 1 hr (see Figure 11). An additional hour of processing produced no further removal. At 350°C, the residual chloride concentration was slightly higher, about 0.03 w/o. In the latter case, the initial chloride value was 0.8 w/o. Experiments with two HF levels, 20 and 50 v/o, gave similar chloride removals, showing no apparent effect of reactant concentration. Since residual chloride values in the bed after fluorination have been in the region of 0.01 w/o, it may be concluded that hydrofluorination at either 400 or 350°C for 1 to 2 hr with 20 v/o HF would be sufficient to lower the chloride content of the fluidized bed sufficiently so that further removal of chlorine during fluorination would be negligible.
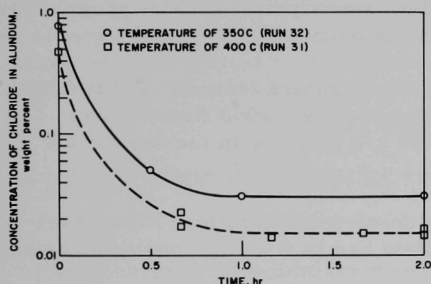
Figure 11

HYDROFLUORINATION OF RESIDUES FROM CHLORINATION STEP - EFFECT OF TREATMENT TIME ON CHLORIDE CONTENT OF THE FLUIDIZED BED

50 m/o HF in the gas stream
Chlorination Conditions: 400 ± 25°C; HCl followed by COCl$_2$

108-7374

VI. THE FLUORINATION STEP

The main objective of this process development work was to establish operating conditions for achieving high (99%) recoveries of uranium. Uranium losses consisted mainly of the uranium in the exit gas from the packed-bed filter during hydrochlorination, and that retained by the alumina beds at the end of fluorination. Hydrochlorination conditions were established that minimized the uranium losses through the filter to less than 0.1% of that in the fuel charge (see page 29). In the following presentation, fluorination procedures that result in an acceptable level of uranium retention by alumina, < 1% of that in the fuel charge, are discussed. Generally, this level of retention corresponded to a final concentration of uranium in the alumina bed of < 0.01 w/o.

During this investigation, 28 experiments (see appendix for summary of experimental data) were performed and six different fluorination schemes were evaluated. These schemes explored the effects of fluorine concentration, time, and temperature as detailed below:

1. One temperature level, 350, 400, 500, or 550°C, fluorine concentration continually increased, up to 90%, as long as isothermal conditions were maintained.

2. Two temperature levels, 250 and 500°C, or 350 and 500°C, treatment at low temperature followed by treatment at high temperature:

    a. Fluorine concentration increased, up to 90%, as long as isothermal conditions were maintained.

    b. Two levels of fluorine concentrations, 50 and 90%, were maintained at each temperature.

    c. Fluorine concentrations were increased in a programmed scheme from 5 to 95% at each temperature.

3. Programmed increase in temperature from (a) 250 to 500°C or (b) 250 to 400°C at constant, low (~10%) fluorine concentration; cleanup with 90 v/o fluorine in the feed at the higher temperature.

Most of the fluorination periods were of 4-hr duration. The feasibility of maintaining the alumina of fluid bed in a static condition during the cleanup period was also tested.

For ease of reporting, typical effects of fluorination conditions are illustrated by a single set of data. The remaining experimental data were consistent with those reported.

A. Effect of Fluorination Procedure on the Recovery of Uranium from Alumina

The effect of fluorination conditions on uranium recovery from the alumina beds was ascertained solely on the basis of the quantity of uranium retained by the alumina in the fluid bed. Since the fluid bed was easier to sample than the packed-bed filter and further, results showed the final concentration of uranium in the filter bed was always less than that of the fluid bed, only fluid-bed analyses were used for evaluation of experiments.

Satisfactory results were obtained in the experiments in which the programmed-temperature scheme (scheme 3a above) and the temperature scheme with temperatures of 250 and 500°C were used. Residual concentrations of uranium in alumina were consistently < 0.01 w/o. In the one-temperature scheme (scheme 1 above), even at a relatively high temperature, 550°C, the alumina bed still contained 0.05 w/o uranium. In the two-temperature scheme, where temperatures of 350 and 500°C were used, the best value was about 0.02 w/o uranium in alumina.

Detailed results of a programmed-temperature fluorination are presented in Table III. The temperature of the fluid bed was gradually increased from 250 to 500°C over a period of 4 hr with 10 v/o influent fluorine. The concentration of uranium associated with the alumina of the fluid bed gradually decreased from 0.57 to 0.05 w/o. The concentration of fluorine was then increased, first to 50 v/o for 1 hr, and then to 90 v/o for an additional hour. The concentration of uranium associated with the alumina decreased further to 0.01 w/o. These data also show the effect of fluorine concentration, alone, in that additional uranium was removed from the alumina by increasing the fluorine concentration from 50 to 90 v/o. The alumina in the reactor was fluidized throughout the run. Maintaining the alumina in a static condition by feeding fluorine at low rates during the cleanup period resulted in similar low values, ~0.01 w/o for the concentration of uranium.

Table III

FLUORINATION OF RESIDUES FOLLOWING HYDROFLUORINATION

Effect of Programmed Increase in Temperature

Fuel Charge: Two miniature multiplate fuel element subassemblies (148 g each) with ~2.1 w/o uranium

Reaction Bed: 320 g of fused alumina -80 + 100 U.S.S. mesh

Fluorination Time (hr)	Temperature (°C)	Maximum Concentration of Fluorine (v/o)	Residual Uranium in Fluid Bed (w/o)
0	250	10.0	0.58
0.5	250	10.0	0.28[a]
1.0	325	10.0	0.17
2.0	400	10.0	0.13
3.0	500	10.0	0.09
4.0	500	10.0	0.05
5.0	500	50.0	0.03
6.0	500	90.0	0.01

[a]Interpolated value.

Conducting a fluorination at two temperature levels, 250 and 500°C, with gradual increase in fluorine concentration from 5 to 90 v/o at each temperature level, was also effective in reducing the concentrations of

uranium retained by alumina at the end of fluorination to less than 0.01 w/o (see Figure 12). The concentration of uranium decreased from 1.0 to 0.04 w/o during the first 2 hr at the lower temperature and decreased finally to 0.005 w/o during the subsequent 2 hr at the higher temperature.

Figure 12

FLUORINATION OF RESIDUES FROM HYDROFLUORINATION - EFFECTS OF GRADUAL INCREASE IN THE CONCENTRATION OF FLUORINE

FUEL CHARGE: TWO MINIATURE MULTIPLATE FUEL ELEMENT SUBASSEMBLIES (137g. each) WITH ~1.9 w/o URANIUM & 13.7g OF SIMULATED FISSION PRODUCTS
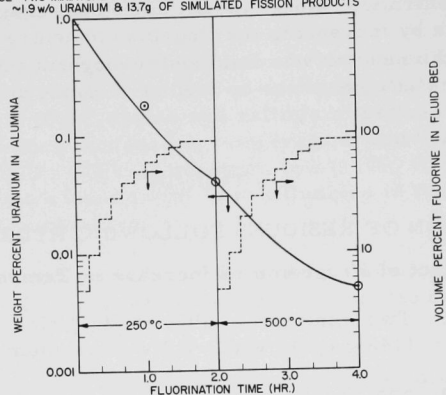
108-7645

Prolonged fluorinations did not appear to improve uranium recoveries. Experimental data indicated that at any temperature (in the range of 250 to 500°C) and fluorine concentration (in the range of 5 to 95 v/o) the concentration of uranium retained by alumina approached an equilibrium value within the first 2 hr; prolonged fluorination, to 18 hr, did not further reduce the concentration of uranium.

In any of the schemes, fluorine recycle may be used to improve the fluorine utilization efficiency. Another method of improving the fluorine utilization is to feed fluorine at low rates and maintain the alumina bed static during the cleanup period. The results from fluorination of static beds show that this operation is satisfactory with regard to recovery of uranium, and beds did not agglomerate or cake. However, radial temperature gradients may result due to the presence of fission products in static beds of alumina. The suitable fluorination scheme may be selected after a critical analysis of the process.

1. Overall Analysis of the Effect of Operating Conditions on Uranium Retained by Alumina at the End of Fluorination. To establish the effects of all the process operating conditions (including hydrochlorination and hydrofluorination conditions) on uranium retained by alumina at the end

of fluorination, a stepwise regression analysis of the data was performed at the end of this investigation. Nineteen variables were tested. Included were such items as reaction temperatures, mass velocities, size and type of alumina, and the partial pressure of UF_6 produced during fluorination.

Results of this analysis, which involved 39 sets of experimental data, indicate that those conditions that tended to decrease the partial pressure of UF_6 in the gas stream resulted in lower retention of uranium by alumina. For example, lowering of the temperature to 250°C during fluorination resulted in lower fluorination rates and hence lower partial pressures of UF_6. Specific hydrochlorination conditions may also have produced such an effect, as follows: a form of uranium chloride which reacts slowly with fluorine may have been produced during hydrochlorination; reaction of this material during fluorination results in lower UF_6 partial pressures in the gas stream. The analysis showed that lowering the temperature of the fluid bed, the mass velocity of the gas stream, and the average hydrochlorination rate of the uranium in the alloy resulted in lower retention by alumina. The rate of reaction of UF_6 with the bed material appears to be a second-order effect, while the moisture content of the HCl appears to have no effect.

More detailed results of the effect of process operating conditions, along with a more accurate relationship between UF_6 partial pressures and uranium retention, will be presented in the forthcoming report on studies with uranium-aluminum alloy fuels, ANL-6830.

VII. OVERALL PROCESS CONSIDERATIONS

Such factors as the distribution of uranium, the distribution of minor constituents of Zircaloy-2 and simulated fission products, the behavior of alumina, and the corrosion of the apparatus over the entire reaction cycle must be known in the development of the reprocessing scheme. Also, over-all flowsheets for the conceptual process are presented (see paragraph F below.

A. Uranium Distribution

A method for evaluating the overall results of an experiment requires accurate knowledge of the distribution of uranium in the process streams. High recovery of the product as UF_6 is also desirable since this satisfies an overall objective of the process. While the uranium recoveries were being determined, a problem existed in that, as a result of current fuel fabrication techniques, the fuel alloy plate was of varying uranium content; the uranium content of the alloy charge, was therefore, not accurately known in the subassemblies. Alloy fuel chips were found to be of uniform composition and were therefore employed in base-line runs. A typical run with alloy chips containing 36.2 g of uranium is summarized in the first column of Table IV. Material balances, as determined from the total of uranium contents of the traps, the two off-gas streams, and solid wastes, were found to be consistently good, near 100%. In subsequent runs with fuel subassemblies, the total of uranium contents in these various sources was taken to be equal to the uranium in the initial charge, since good uranium balances were obtained in runs with chips. Distribution of uranium for a typical multiplate subassembly run is shown in column 2 of Table IV. These two runs, made under quite different conditions, showed similar low uranium losses and high uranium recoveries.

B. Distribution of Minor Constituents and Simulated Fission Products

Volatilization of some of the fission products and/or the minor constituents of Zircaloy-2 during all the steps in the process is expected. Information on the disposition of these elements is important in the design of the UF_6 purification system, the pyrohydrolysis equipment for the waste zirconium tetrachloride stream, and the solid waste storage system. To obtain this information, mixtures of inactive fission products were added to the reactor along with the alloy charge. In one experiment, uranium-Zircaloy-2 alloyed with fission products was processed. The composition of the fission product mixture was similar to that calculated by Burris and Dillion[9] for U^{235} with 150-day irradiation and 30-day cooling. Eleven fission products* with concentrations greater than that of antimony (0.027 g of antimony per 100 g of U^{235}) and with specific activities greater than that

---

*Strontium, yttrium, niobium, molybdenum, ruthenium, rhodium, antimony, tellurium, cesium, barium, and cerium.

of molybdenum (2.3 Curies/g) were represented. Lanthanum and rare-earth elements, except cerium, were not added. The total concentration of fission products added ranged from 1.5 to 4.2 w/o of the alumina in the fluid bed (320 g).

Table IV

URANIUM DISTRIBUTION IN PROCESS STREAMS

Fluid Bed: 320 g of fused alumina
Packed-bed Filter: 320 g of fused alumina
Superficial Velocity of Gas: ~0.7 ft/sec (at column conditions)

Alloy Charge, g	721.0 (5.02 w/o uranium, chip form)	296.0 (~2 w/o uranium, subassemblies)
Uranium Recovered	% of Charge	% of Total Found
1. UF$_6$ product recovered from cold traps	98.2	96.9
2. UF$_6$ recovered from activated alumina trap	0.5	0.1
3. Uranium in bed samples	0.7	2.1
Total Uranium Recovered	99.4	99.1
Uranium Lost		
1. Uranium retained by alumina		
a. In fluid bed	0.14	0.53
b. In packed-bed filter	0.29	0.32
2. Uranium loss through packed-bed filter during hydrochlorination	0.29	0.03

The relative distributions of most of the minor constituents in Zircaloy-2 and the fission products, as determined by X-ray spectrographic and spectrochemical analyses, were in conformity with the distributions estimated from the volatilities of their higher-valent chlorides and fluorides. A major amount (~95%) of the tin, but only a small portion (11%) of the iron, were volatilized during hydrochlorination. Molybdenum and niobium were found to be distributed among the $ZrCl_4$ condenser, the UF$_6$ condenser, and the reactor. A portion (33%) of the chromium was volatilized during the fluorination with fluorine. The detailed distributions of these elements along with those for boron, lead, manganese, and silicon are reported in Table V. Seven of the elements, silver, barium, cerium, cadmium, cobalt, strontium, and yttrium, remained with the alumina in the fluid bed and the

packed-bed filter. Five of the fission products (ruthenium, rhodium, antimony, tellurium, and cesium) charged could not be detected due to the insensitivity of the analyses. Although appreciable information is now available on the distribution of these elements, work with irradiated fuel sections is being carried out to confirm these data.

Table V

DISTRIBUTION[a] OF SPECIFIC FISSION PRODUCTS
AND MINOR ELEMENTS

Simulated Fission Product Charges: 4.8 to 13.7 g

Element Symbol	Percent Volatilized			Percent Nonvolatile Retained by Fluid and Filter Beds
	During Hydrochlorination	During Hydrofluorination	During Fluorination	
Elements added as fission products				
Mo	21	b	76	3
Nb	44	6	23	27
Elements present in Zircaloy-2 charge				
Cr	7	10	33	50
Pb	b	12	21	67
Sn	95	b	1	4
Elements present in Zircaloy-2 charge and contaminants from constructional materials				
B	61	1.0	17	21
Fe	11	1	14	74
Mn	18	3	20	59
Si	7	b	4	89
Ti	b	b	53	47

[a]Average values based on two experiments. Distribution percentages are based on the total amount found.
[b]None detected.

C. Behavior of Alumina

High-fired alumina (both fused and sintered types) was found to be a satisfactory inert bed material. Its stability as regards caking tendencies was tested in a group of experiments in which planned interruptions were carried out during and after each reaction step of the processing cycle. The interruptions during the reaction steps consisted of a) stopping the gas flow (causing the fluid bed to become static), b) rapidly cooling the reactor from its operating temperature to room temperature, c) maintaining the reactor at room temperature for 2 hr, and d) reheating the reactor to the operating temperature. Planned interruptions after the reaction step involved a) stopping the gas flow, b) heating the reactor assembly (fluid-bed reactor and packed-bed filter) to 600°C, c) maintaining the assembly at 600°C for 2 hr, and d) cooling from 600°C to the normal operating temperature.

The alumina in the fluid bed did not cake or agglomerate during any of the interruptions, and the material was readily refluidized upon startup of the gas flow and also drained readily from the reactor after the experiment was completed. No caking occurred in the alumina packed-bed filter.

Some changes in the physical nature of the alumina in the fluid bed were noted, although these changes did not appear to affect the overall results. At the end of a reaction sequence, particles were found to be coated with solid reaction products, and some attrition of the alumina was noted. Particle growth was observed by a small increase in the quantity of +30 mesh particles, the increase in particle size being due to the reaction products coating the alumina (see Table VI). About 11 w/o of the alumina in the final bed was smaller than the starting bed size, indicating that some attrition occurred. The physical properties of the alumina used in this investigation are reported in the appendix.

Table VI

SCREEN ANALYSIS OF FLUID-BED ALUMINA
BEFORE AND AFTER REACTION CYCLE

Fluid-bed Charge: 320 g of sintered alumina

Air Gas Velocity: ~0.7 ft/sec

Fuel Charge: Two miniature multiplate fuel element subassemblies (137 g each) with ~1.9 w/o uranium; 13.7 g of simulated fission products.

Reaction Cycle:

Reaction	Temperature (°C)	Time (hr)
Prefluorination	500	1
Hydrochlorination	350	8.0
Hydrofluorination	350	2.0
Fluorination	250-500	4.0

Mesh Size	Initial Alumina Charge, % in Given Size	Alumina after One Reaction Cycle, % in Given Size
+30		4.7
-30 +40	26.4	23.7
-40 +50	53.9	47.1
-50 +60	19.7	13.4
-60 +120		4.7
-120 +200		2.6
-200 +325		1.6
-325		2.2

D. Performance of the Packed-bed Filters

Packed beds of alumina are being used as high-temperature filters for gas streams carrying particulate matter during both hydrochlorination and fluorination because of their simplicity in operation and because of the

inertness of the material. The pressure drop for flow of gases through these packed-bed filters affects the total pressure on the reactor system and causes a possible change in the reaction mechanism. From an operational standpoint, high back pressure on the inlet reactant gases is undesirable.

Pressure buildup across the packed-bed filters was noted in the early studies of this investigation. The increased pressure drop across the filter was caused by the deposition of fine particulate matter on the packed bed. These fines had been produced in the main reactor and entrained over to the filter section by the off-gas stream. The particulate material was identified as $NiCl_2$, UCl_3, UCl_4, ZrO_2, and alumina. The quantity and quality of the particulate material were dependent on hydrochlorination conditions. As the temperature of the fluid-bed reactor walls was increased above 400°C, more $NiCl_2$ was produced; similarly, as the temperature drop between the fuel reaction surface and the fluid bed was increased, more uranium chloride particulate solids resulted and were collected on the filter. The ZrO_2 was produced from reaction of the impurities, oxygen, and H_2O, in the feed gas stream with either zirconium or $ZrCl_4$. Also, the oxygen in the fuel might have contributed to the quantity of ZrO_2 collected on the filter. The pressure drop was found to decrease slightly upon fluorination as the uranium chlorides were converted to UF_6. The pressure buildup problem was alleviated by increasing the particle size of alumina from 0.125 (nominal 120 mesh size) to 1.4 mm (nominal 14 mesh size).

The observed pressure drops for flow of gases through the packed-bed filter were similar to the pressure drops that may be estimated from the correlation proposed by Leva et al.[39] Moreover, the correlation indicates the following three criteria for decrease in the pressure drop, which were found to be true with the high-temperature packed-bed filter. The pressure drop for flow of gases through the packed-bed filter decreases with

a) Increase in the diameter of the particles,

b) Increase in the void fraction of the bed, and

c) Decrease in the temperature (due to the decrease in the viscosity of the gases).

E. Corrosion

Preliminary information on corrosion of nickel during processing cycles was obtained (see Table VII). Nickel is considered as the likely material of construction. Corrosion coupons mounted in the fluid-bed zone and in the disengaging zone were exposed to reactant and product gas streams over a period of about 200 hr (11 runs). The average corrosion rates were less than 60 mils/yr, and intergranular corrosion was not observed. The corrosion rates were ~0.15 and 0.2 mil/run for specimens in

the disengaging zone and the fluid-bed zone, respectively. Actual measurements of the inside diameter of the fluid-bed reactor corroborate these results. The corrosion rates were similarly low for various reaction sequences.

More accurate corrosion data will be reported in ANL-6979 (see page 3).

Table VII

CORROSION DATA ON NICKEL-200 SPECIMENS[a]

Average corrosion rates: <60 mils/yr

No intergranular corrosion. Note the similarity in corrosion rates with the various reaction sequences.

Average reaction cycle conditions:

Reactant	Temp (°C)
HCl	400
COCl$_2$	350
HF	350
F$_2$	250-500

Run No.	Reaction Time (hr)				Corrosion Rates (mil/cycle)	
	HCl	COCl$_2$	HF	F$_2$	Specimen in the Fluid Bed	Specimen in the Disengaging Chamber
1	6	1	3	4		
2	21	1	2	8	0.21	0.14
3	6		2	6		
4	21		2	8		
5	7			4		
6	14			6	0.19	0.16
7	13		2	6		
8	10		1	5	0.24	0.16
9	8		1	4		
10	11		1	15	0.2	0.15

[a]Nickel-200 tube sections (1 in. high, 1/4-in. diam., weighing ~3.2 g) were hung in the fluid bed and in the disengaging chamber.

F. Flowsheets

Experimental data indicate that considerable flexibility exists in this process and a number of flowsheets could be devised. One concept calls for recycle of process gas; recycle would further reduce the already low reactant requirements of a once-through scheme. Possible process improvements through recycle are discussed in paragraphs 1 and 2.

1. Hydrochlorination. The gas stream from the reactor in which the fuel is hydrochlorinated is fed to a fluid-bed pyrohydrolysis reactor for the disposal of $ZrCl_4$ as ZrO_2 (Figure 13). The off-gases from the fluid-bed pyrohydrolysis reactor may then be fed to a condenser maintained at 21°C [equilibrium moisture content of 1100 ppm[40]] for the recovery of HCl. The HCl gas stream from the condenser may then be recycled. A certain fraction of this gas stream would be bled to limit the amount of hydrogen and inerts in the feed gas to the fluid-bed hydrochlorinator and to remove all the hydrogen produced in the process. The bleed stream could be scrubbed by the feed water to the pyrohydrolysis reactor to recover part of the HCl. The remaining HCl in the bleed stream could be scrubbed (optional scrub system, Figure 13) with dilute hydrochloric acid (20.3 w/o HCl azeotrope). The exhaust hydrogen would then contain only 0.03 v/o HCl. With this scheme, the concentrated acid is fed to a stripper-condenser combination. The HCl leaves the top of the condenser, which is maintained at 21°C, and is fed back to the hydrochlorinator as make-up HCl, while the

Figure 13

SUGGESTED FLOWSHEET FOR THE HYDRO-
CHLORINATION STEP FOR PROCESSING
URANIUM-ALLOY FUELS
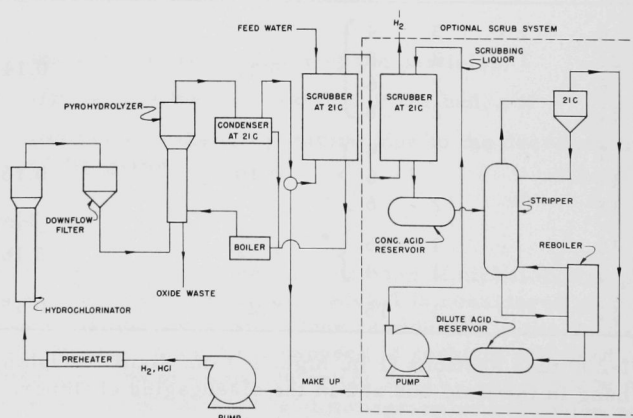
dilute hydrochloric acid (azeotrope) from the bottom of the stripper is pumped back to the scrub tower as scrubbing liquor. Under ideal conditions, the recycle of the gas stream, coupled with the optional scrub system, results in a hydrochlorination step with only 0.0006 mole of HCl required per mole of zirconium alloy processed. The optional scrub system is similar to the commercial HCl recovery process.[41,42] The process equipment may be made of tantalum or impervious graphite.

　　　2. Hydrofluorination and Fluorination. In the hydrofluorination and fluorination steps, the main gas stream may be recycled after a certain portion is bled to maintain the desired concentration of the reactant in the feed gas stream to the fluid-bed reactor. Figure 14 shows a suggested flowsheet for these steps. Experience and technology on such operations have been obtained in fluoride volatility studies.
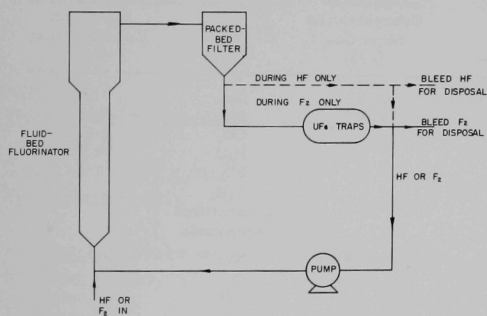
Figure 14

SUGGESTED FLOWSHEET FOR THE HYDROFLUORINATION AND FLUORINATION STEPS FOR PROCESSING URANIUM-ALLOY FUELS

VIII. CONCLUSIONS

　　　A fluid-bed volatility process scheme that gives consistent recoveries of greater than 99% of the uranium from normal uranium-Zircaloy-2 alloy charges has been developed. The process is also applicable to aluminum-based fuels, as will be discussed in forthcoming report ANL-6830.

　　　The process development studies, conducted in a $1\frac{1}{2}$-in.-diam. fluid-bed system, indicate that: a) appreciable flexibility in reaction conditions exists for each of the major reaction steps, hydrochlorination, hydrofluorination, and fluorination; b) economic advantage of this process over others is expected because the equipment is simple, only commercial-grade reagents are needed, and the quantity of radioactive wastes produced is relatively small; and c) corrosion rates are low for the nickel-200 equipment used (preliminary data show that rates lower than 60 mils/yr were sustained during the current development studies on zirconium alloy fuels). Process scale-up to plant level for processing enriched uranium-alloy fuel assemblies appears very promising.

APPENDIX

Supplementary Information

A. Analyses of Gases and Inert Bed Materials

Commercial-grade chemicals were used throughout the current process development work. Typical compositions of commercial-grade gases are listed in Table VIII. The types of alumina used as inert bed material in the current work are described in Table IX.

Table VIII

COMPOSITION OF GASES USED IN CURRENT WORK

| | | Composition Guaranteed by Manufacturer | | |
| | | | Typical Impurities | |
Gas	Name of Manufacturer	Minimum Concentration Main Gas (v/o)	Gas	Maximum Concentration (v/o)
N_2	Air Products and Chemicals	99.997	O_2	0.003
HCl	Matheson Company	99.0	Air	0.2
			CO_2	0.5
			H_2O	30 ppm
			SO_2	
			C_6H_6	~0.3
			Unidentified Compounds	
H_2	Liquid Carbonic	99.95	N_2	40 ppm
			O_2	1 ppm
			CO	60 ppm
			CO_2	8 ppm
			CH_4, etc.	100 ppm
			H_2O	35 ppm
Cl_2	Matheson Company	99.5	CO_2	0.5
			O_2	0.04
			N_2	0.07
			CCl_4, etc.	40 ppm
			$FeCl_3$, etc.	25 ppm
$COCl_2$	Matheson Company	99	Cl_2	0.1
			HCl	0.2
			CH_3COOH	0.1
			Unidentified	0.6
F_2	General Chemical Division Allied Chemical & Dye Corporation	98.5	O_2	0.2
			N_2	0.7
			HF	0.1
			CF_4	
			SiF_4	0.5
			CO_2	
Standard Gas Mixtures of $N_2 + H_2$ and $N_2 + Cl_2$	Matheson Company		O_2	0.2
HF	Harshaw Chemical Company	99.96	SiF_4	0.006
			SO_2	0.007
			H_2O	0.019
			$H_2SO_4 +$ $HFSO_3$	0.005

Table IX

TYPICAL PROPERTIES OF ALUMINA USED IN BED MATERIALS

| Constituent, w/o | Fused Alumina (Alundum[a]) | | Sintered Alumina |
	Type RR (Blue Label)	Type 38	Tabular, Type T-61[b]
Al_2O_3	99.5+	99.49	99.5+
SiO_2	<0.01	0.05	0.06
Fe_2O_3	0.03	0.10	0.06
Na_2O	<0.02	0.35	0.03
Uranium	0.0003	0.0005 to 0.0009	0.0004
Property:			
Bulk density, packed, lb/cu ft	116	116	135
True density, g/ml	3.96	3.96	3.96
Specific gravity	3.89	3.87	3.65 to 3.8
Hardness (Mohs scale)	Not available	9	9
Melting point, °C	2000	2000	2040
Cost,[c] ¢/lb	69	33	14

[a]Manufactured by Norton Company, Worchester 6, Massachusetts.
[b]Manufactured by Aluminum Company of America, Bauxite, Arkansas.
[c]Costs based on 100-lb lots.

B. Summary of Experimental Data

All the experimental data obtained in this investigation on the chlorination-fluorination of uranium-Zircaloy-2 alloy fuels are summarized chronologically in Tables X to XII. The initial experiments (Runs 2 to 13, Table X) on the hydrochlorination step were conducted to evaluate the performance of the high-temperature packed-bed alumina filters with respect to the quantity of uranium retained on the alumina bed. The subsequent experiments (Runs 14 to 42) were made to determine the optimum operating conditions. This set of experiments is divided into two series. In the first series (Runs 14 to 25), modifications in the operating conditions of the basic hydrochlorination-fluorination cycle were studied. In the second series (Runs 26 to 42), variations in the reactant sequence were evaluated. The sequences were: $HCl - F_2$, $HCl - COCl_2 - F_2$, $HCl+COCl_2 - COCl_2 - F_2$, $HCl - COCl_2 - HF - F_2$, $HCl - HF - F_2$, $H_2+Cl_2 - HF - F_2$, HCl with various moisture

contents - HF - F_2. The data on the hydrochlorination and fluorination steps are presented in Table XIIa; the data on the additional intermediate steps are given in Tables XIIb and XIIc.

Table X

HYDROCHLORINATION OF URANIUM-ZIRCALOY-2 ALLOY FUEL

Summary of data from runs to evaluate the design of packed-bed filters;
Fuel charge: chips, 1/4 to 1/8 in. on a side

	Fuel Charge		Reaction Bed		Packed Bed		Hydrochlorination				
Run No.	Wt. (g)	Conc. U (w/o)	Wt. (g)	Avg. Mesh Size	Wt. (g)	Avg. Mesh Size	Time (hr)	Avg. Fluid-bed Temp (°C)	Avg. Packed-bed Filter Temp (°C)	HCl Quantity x Stoichiometric	% U Loss[a]
2 Up-flow	107	5.0	780	120[b]	2060	120[b]	2.2	400	400	2.6	1.5
3 Up-flow	172	2.8	870	120	1970	120	4.0	370	370	4.4	0.3
4 Up-flow	158	2.7	1000	120	1800	120	5.0	360	390	11.7	0.6
5 Up-flow	151	2.7	550	30	160	30	4.0	360	390	6.1	0.6
6 Down-flow	278	2.7	550	120	1940	120	5.3	350	400	4.2	0.3
7 Down-flow	257	2.7	550	60	910	140	5.1	360	360	3.5	0.3
8 Down-flow	229	2.7	550	60	1870	140	5.0	360	450	4.8	0.2
9 Down-flow	257	2.7	550	60	2660	140	4.4	360	400	2.8	0.2
10 Down-flow	266	2.7	550	60	2060	80	5.3	390	400	2.9	0.1
11 Down-flow	267	2.7	550	60	600	120	5.0	360	420	4.2	0.1
12 Down-flow	263	2.7	550	60	840	120	5.0	370	430	4.3	0.8
13 Down-flow	118	2.7	550	60	860	70	3.8	360	400	4.5	0.2

[a]Uranium loss is the sum of the percentage of uranium found in the $ZrCl_4$ condenser and the HCl disposal tower.
[b]Estimated.

Table XI

HYDROCHLORINATION AND FLUORINATION OF URANIUM-ZIRCALOY-2 ALLOY FUEL

Effects of operating conditions on uranium recoveries;
Fuel charge: chips, 1/4 to 1/8 in. on a side

	Fuel Charge		Fluid Bed		Packed Bed		Hydrochlorination						Fluorination			Residual U Content of Alumina (w/o)	
Run No.	Wt. (g)	Conc. U (w/o)	Wt. (g)	Avg. Mesh Size	Wt. (g)	Avg. Mesh Size	Time (hr)	Avg. Fluid-bed Temp (°C)	Avg. Packed-bed Filter Temp (°C)	HCl[a] Quantity x Stoichiometric	% U Loss	Temp (°C)	Time (hr)	Max. Fluorine Partial Pressure (atm)	Fluid Bed	Packed-bed Filter
14	362	2.7	550	90	865	140	5.0	370	430	3.0	0.14	350	10.5	0.52	0.043	0.012
15	225	2.7	550	90	865	100	3.6	375	400	3.0	0.17	350	0.1	0.50[b]	c	c
16	272	4.8	2800	90	380	50	6.0	385	400	3.5	0.11	350	6.0	0.76	0.016	0.015
17	341	4.8	2000	90	370	50	5.8	390	370	3.4	0.05	350	6.0	0.72	0.052	0.019
18	339	4.8	550	90	1450	60	4.0	400	370	1.8	0.22	350	8.2	0.64	0.60	0.036
19	350	4.8	550	90	370	60	8.7	370	370	2.9	0.12	350	5.6	0.99	0.060	0.026
20	345	4.8	550	90	370	60	5.5	390	360	2.4	0.04	350	6.0	1.16	0.033	0.021
21	349	5.0	550	90	370	60	6.5	370	350	2.2	0.25	350	5.5	1.16	0.10	0.06
22	350	5.0	550	90	320	70	16.0	365	350	2.5	0.10	350	16.8	1.13	0.10	0.071
23	350	5.1	550	60	320	50	5.0	450	440	4.0	0.05	350	6.0	0.86	0.061	0.045
24	350	5.1	550	60	360	50	6.5	500	550	4.0	0.05	550	6.0	0.98	0.05	0.031
25	240	5.1	320	50	c	c	12.5	500	c	11.0	0.88	500	9.8	0.82	0.03	c

[a]Moisture content of HCl was 35 ppm.
[b]Estimated.
[c]Data not available.

TABLE XII

HYDROCHLORINATION AND FLUORINATION OF URANIUM-ZIRCALOY-2 ALLOY FUEL

a. Runs Made with Variations in the Basic Reactant Sequence;
Fuel charge: chips, 1/4 to 1/8 in. on a side for Runs 26 to 34. Miniature multiplate fuel element subassemblies for Runs 37 to 42.

Run No.	Fuel Charge Wt. (g)	Fuel Charge Conc. U (w/o)	Fluid Bed Wt. (g)	Fluid Bed Avg. Mesh Size	Packed Bed Wt. (g)	Packed Bed Avg. Mesh Size	Hydrochlorination Time (hr)	Avg. Fluid-bed Temp (°C)	Avg. Packed-bed Temp (°C)	HCl Quantity x Stoichiometric	% U Loss	Fluorination Part 1 Temp (°C)	Part 1 Time (hr)	Part 2 Temp (°C)	Part 2 Time (hr)	Max. Fluorine Partial Pressure (atm)	Residual U Content of Alumina (w/o) Fluid Bed	Packed-bed Filter
26	240	5.1	320	90	a	a	17.0	400	a	13.0	1.57	400	7.7	500	2.0	1.07	0.03	a
27	240	5.1	320	90	a	a	28.0	400	a	25.0	0.97	400	6.9	500	9.5	0.88	0.03	a
28	240	5.1	320	90	a	a	7.0	400	a	11.0	0.35	400	16.0	500	2.0	0.88	0.017	a
29	240	5.1	320	90	a	a	2.5	400	a	8.0	49.5	400	8.7	-	-	0.84	0.04	a
30	240	5.1	320	90	320	40	4.8	400	400	5.0	5.1	400	5.4	500	2.0	0.78	0.02	0.029
31	240	5.1	320	90	300	40	1.0	400	400	5.0	0.44	400	2.0	500	2.0	1.02	0.05	0.014
32	720	5.0	320	90	320	30	15.0	400	400	3.0	0.22	350	2.0	500	2.0	0.70	0.025	0.029
34	320	5.1	320	90	320	40	6.0	400	420	4.0	0.03	350b	2.0	500b	6.0	0.64	0.03	0.017
35	720	5.0	320	90	320	30	20.5	400	400	4.0	0.06	350	2.0	500	6.0	0.86	0.05	0.015
37	160	1.0	320	90	320	20	7.3	400	410	5.0	2.20	250b	2.0	500b	2.0	0.81	0.010	0.007
38	367	1.1	320	90	320	20	13.6	350	350	8.7	0.03	250	2.0	500	0.5	1.08	0.01	0.004
39	296	2.1	320	90	320	20	10.5	400	340	9.0	0.02	250b	3.0	250 to 500b	4.0d	0.90	0.01	0.006
40c	281	1.0	320	70	320	20	14.7	375	350	4.6	0.09	250	2.0	500	2.0	1.16	0.013	0.016
41	274	1.0	320	40	320	20	8.0	410	330	2.8	0.02	250	2.0	500	2.0	1.45	0.008	0.006
42	411	4.0	320	50	320	25	11.0	400	350	2.9	0.02	250 to 500	4.0	500	11.0	1.27	0.01	0.01

a No filter used.
b Filter and reactor beds fluorinated separately.
c Included simulated shutdowns.
d Reactor bed fluorinated for 25 additional hours.

c. Variations in the Basic Reactant Sequence;
Treatment with Hydrogen Fluoride
Concentration of HF in Feed Gas: 50 v/o for all runs except for the first hour of Run No. 39, during which it was 20 v/o.

b. Variations in the Basic Reactant Sequence;
Treatment with Phosgene

Run No.	Moisture Content of HCl (ppm)	Phosgene Time (hr)	Fluid-bed Temp (°C)	Packed-bed Filter Temp (°C)	COCl2 Quantity x Stoichiometric
28	1.0	8.2	400	a	7.0
29	1.0	5.5	400	a	5.4
30	1.0	6.5	400	400	2.0
31	1.0	1.0	400	400	2.0
32	1.0	1.0	350	350	0.5

a Packed-bed filter was not used.

Run No.	Hydrofluorination Moisture Content of HCl (ppm)	Time (hr)	Temperature of Fluid Bed and Packed-bed Filter (°C)
31	1.0	2	400
32	1.0	2	350
34a	1.0	2	350
39a	1100	2	350
40b	1100	1	350
41b	1100	1	350
42c	1100	1	350

a Hydrogen was fed along with HCl.
b Fission products were charged along with the fuel.
c Uranium-Zircaloy-2 alloyed with fission products was processed.

Fused alumina manufactured by Norton Company was used in all the runs except the last two (41 and 42) in which sintered alumina manufactured by Aluminum Company of America was used. Two types (low-purity Type 38 and high-purity Type RR) of fused alumina were used and both were satisfactory in performance. Since the differences in the performance of the three types of aluminas are insignificant, the types used in each run were not included in the summary of experimental data.

C. Continuous Off-gas Analysis with Thermal Conductivity Cells

Thermal conductivity cells (TCC's) are currently providing a means of continuously following the course of the principal reactions (the hydrochlorination and fluorination reactions) in the fluid-bed volatility scheme for reprocessing uranium-zirconium alloy fuels. In this application,

these TCC's detect small differences in the thermal conductivity of two gas streams, a reference stream and the process off-gas stream. The reference gas is usually the unchanging component in the process gas stream against which a change in concentration of a key component in the process stream is referred. By having the TCC calibrated for the particular system, the concentration or change in concentration of one or more of the key components in the off-gas stream is continuously determined. A review of the principles involved in the operation of these TCC's is being presented with the hope of furthering their applications in nuclear fuel reprocessing work. Several suggested ways of using these TCC's and performance data on TCC's being used currently are also given.

1. Relationship between Thermal Conductivity and Other Properties of Polyatomic Gases. The thermal conductivity, k, of a gas or gaseous mixtures is defined by the equation,

$$q_x = -k \frac{dt}{dx}, \tag{1}$$

where q_x is the heat flux,

　　t is the temperature,

and

　　x is the distance in the direction of heat flow.

The thermal conductivity is the energy transport coefficient which is analogous to viscosity, μ, the momentum transport coefficient. These two coefficients are interrelated for polyatomic gases by Eucken's semi-empirical relation,

$$k = (\mu/M)(C_p + 1.25R), \tag{2}$$

where M is the molecular weight, C_p is the molal specific heat at constant pressure, and R is the gas-law constant.[43] The coefficient of viscosity of the polyatomic gases may be estimated by the relation,[44]

$$\mu = 2.6693 \times 10^{-5} \sqrt{MT}/(\sigma^2 \Omega_\mu), \tag{3}$$

where

　　μ is viscosity, in poise;

　　T is absolute temperature, in °K;

　　σ is the collision diameter, in angstroms;

and

　　Ω_μ is the collision integral.

Substituting (3) into (2) gives

$$k = 2.6693 \times 10^{-5} \frac{\sqrt{T}}{\Omega_\mu} \frac{1}{\sqrt{M}} \frac{1}{\sigma^2} (C_p + 1.25R).$$

If consistent metric units are used, the dimensions of k will be cal/ (sec)(cm)(°C). This equation has been presented to show the relationship between thermal conductivity and molecular weight of polyatomic gases but it may be used also as a general equation for estimating the thermal conductivity of polyatomic gases in the absence of experimental data.

Pertinent molecular properties of the gases of interest in the volatility studies are summarized in Table XIII. The thermal conductivity data were taken from Lenoir,[45] DeWitt,[15] and Misic and Thodos.[46] The molecular weights of these gases cover a relatively wide range. There is a corresponding spread in the range of thermal conductivities. For the extreme values of molecular weight, 352 for UF_6 and 2.0 for hydrogen, the corresponding thermal conductivities are 0.004092 and 0.111 Btu/(hr)(ft)(°F). In the current work, since nitrogen is used as a reference gas in the TCC during hydrochlorination and since it makes up a major portion of the nitrogen-fluorine mixture that is used as a reference stream in the fluorination step, the ratio of thermal conductivities of nitrogen to the other gases is also of interest. As shown in Table XIII, these ratios range from 0.14 for nitrogen-hydrogen to 3.8 for nitrogen-UF_6.

Table XIII

SELECTED PHYSICAL PROPERTIES OF GASES USUALLY ENCOUNTERED IN
FLUIDIZATION AND VOLATILITY STUDIES OF NUCLEAR PROCESSES

| Gas	Formula Weight	Boiling Point (°K)	Molal Heat Capacity at Constant Pressure (cal/g mole, °K)	Thermal Conductivity, k, at 100°F (Btu)/(hr)(ft)(°F)	Ratio of Thermal Conductivity of Nitrogen to Thermal Conductivity of Gas
UF_6	352.1	329.6°	31.0	0.004092	3.8
Cl_2	70.9	238.4	8.12	0.0053	2.9
HCl	36.5	188.0	6.96	0.0085	1.8
O_2	32.0	90.0	7.02	0.01595	0.972
F_2	38.0	86.0	7.52	0.0160	0.969
H_2S	34.1	213.5	10.52	0.0089	1.74
N_2	28.0	77.2	6.96	0.0155	1.0
H_2O	18.0	373.0	8.02	0.0108	1.505
He	4.0	4.2	5.0	0.0892	0.174
H_2	2.0	20.4	6.9	0.111	0.14

*Sublimation point.

2. **Analysis of the Construction and Calibration of a Thermal Conductivity Cell.** An analysis of the construction of a TCC and the important principles involved in the operation of these TCC's during the continuous analysis of a gas stream are described below. The main feature of the TCC is the filament or "hot-wire" circuit (see Figure 15). The circuit is in the form of a bridge that contains four (or a multiple of four) identical fixed-resistance elements (filaments) and a variable resistance for zeroing purposes. A dc voltage is applied across the bridge maintaining the filaments at a relatively high temperature, and an indicator and/or recorder

are employed to detect current or voltage changes (the output) in the circuit during operation of the TCC.

Figure 15

SCHEMATIC DIAGRAM OF A DIRECT-CURRENT
BRIDGE CIRCUIT USED FOR MEASURING THE
THERMAL CONDUCTIVITY OF GASES
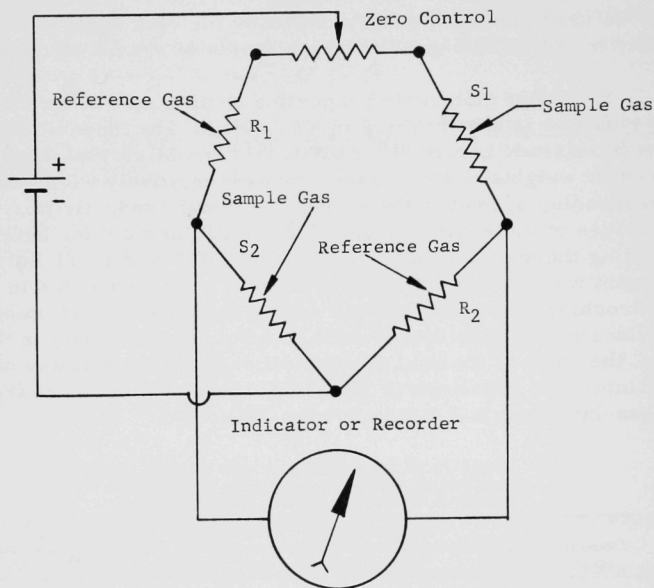
The TCC block, within which the filaments are contained, provides two paths for flowing gases. The reference gas contacts the reference filaments, R_1 and R_2, while the sample gas, whose composition is to be determined, contacts the other set of filaments, S_1 and S_2.

The filaments have a large temperature coefficient of resistance, a property that is fundamental to the operation of the TCC. With the circuit balanced (electrically), and the reference gas flowing in both channels of the block, the temperature of the two sets of filaments will be the same. Passing a gas whose thermal conductivity is different from that of the reference gas through the sample side of the TCC will result in a difference in temperature between the two sets of filaments. This variance in temperature (because of the relation between temperature and resistivity of the filaments) produces an imbalance in the circuit. The extent of the imbalance, noted as voltage output, is a measure of the

difference in thermal conductivities of the reference gas and the sample gas. When the sample gas is a mixture of the reference gas and another component whose presence brought about the imbalance in the circuit, the composition of the sample gas can be readily determined by proper calibration of the TCC.

To calibrate the TCC for a particular process step in which the off-gas constituents will be known, a prepared gas mixture representing an off-gas of known composition is passed through the sample side of the TCC while the reference gas is passed through the reference side. This procedure is repeated with several gas mixtures of known composition in the range of concentrations that may be encountered in the process. The output of the bridge is then plotted against the concentration of the known constituent in the mixture, thereby establishing a calibration curve. The same reference gas that was used for calibration must be used in the actual process application. The process gas stream that is to be analyzed is passed through the sample side.

Several ways of using TCC's are outlined below:

a.   For measuring the concentration of one of the constituents of a binary gas mixture, the major constituent of the mixture may be used as the reference gas, and the gas mixture itself may be used as the sample gas; e.g., for measuring the concentration of hydrogen in nitrogen, nitrogen may be considered as the reference gas, and the gas mixture of nitrogen and hydrogen is then the sample gas.

b.   For following the progress of a reaction that results in a change in concentration of the reactants, the gas mixture at the outlet of the reactor may be used as the sample gas; e.g., during fluorination, the inlet gas containing nitrogen and fluorine may be used as a reference gas; the outlet gas containing the reaction products (UF_6 and chlorine), unreacted fluorine, and nitrogen may be used as the sample gas.

c.   For measuring the concentration of each of the components of a ternary gas mixture, two TCC's may be used as illustrated in Figure 16. The gas mixture with all three of the constituent gases (e.g., water vapor, HCl, and nitrogen) may be considered as the sample gas. The sample mixture is then passed through a trap (either physical or chemical type) which removes one of the gases (e.g., water vapor). The remaining gases may then be used as the reference gas in the first TCC. With proper calibration, the voltage output from the first TCC will then correspond to the concentration of water vapor in the ternary mixture. The gas mixture containing HCl and nitrogen may then be used as the sample gas in TCC No. 2, and after a trapping operation similar to the above situation to remove HCl from this binary mixture, nitrogen becomes the reference gas. Again with proper calibration, the concentration of HCl in the binary mixture can be determined.

Figure 16

USE OF THERMAL CONDUCTIVITY CELLS FOR MEASURING
THE CONCENTRATIONS OF MORE THAN TWO GASES

Thermal Conductivity Cell #1

Thermal Conductivity Cell #2
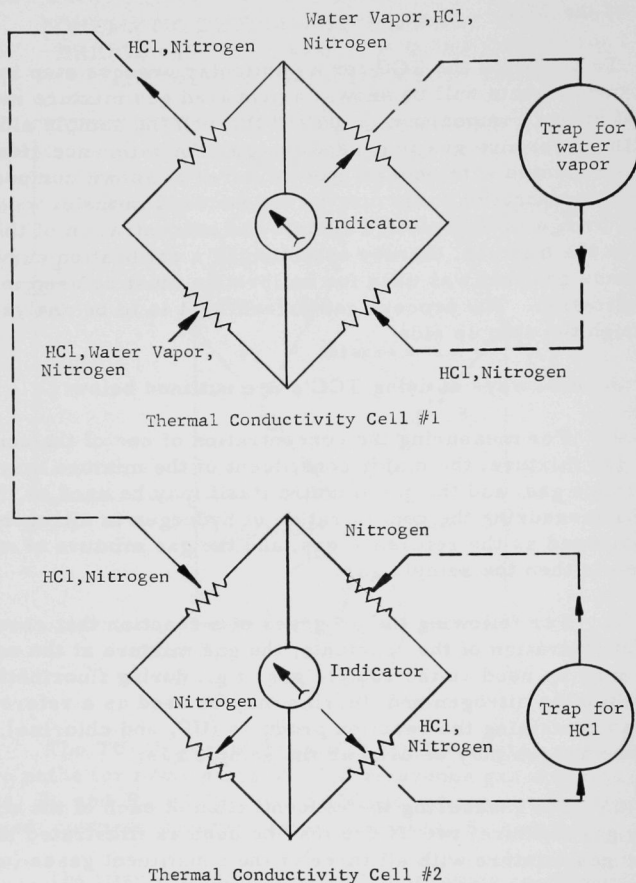
Wide variations in the types of filaments and in the construction
of the TCC block are available, along with a variety of dc power supply
units and recorders. Materials from which filaments have been made
include (1) tungsten, (2) gold-plated tungsten, (3) Teflon-clad tungsten,
(4) "Kovar" (alloy of nickel, cobalt, and iron), (5) nickel, (6) glass bead
thermistors on platinum supports, and (7) platinum-iridium. The TCC
blocks may be fabricated from special materials such as stainless steel,
nickel, and nickel alloys. This list of materials indicates that TCC's can

be built for use where special problems with corrosive process gas streams exist. When the variations in concentrations of a component of the gas stream are small, pairs of filaments are employed instead of single ones. This arrangement of filaments essentially doubles the output and permits the measurement of very small concentration changes. Further, TCC's mounted in a thermostatically-controlled enclosure to maintain the temperature of the gas streams and the cell block at temperatures in the range of 21 to 200°C are available. These cells are especially useful in measuring the concentration of gases that would normally condense at room temperature, e.g., UF_6 (sublimation point, 56.6°C). An indication of cell sensitivity is the fact that cells capable of detecting 10 ppm of helium in nitrogen are available.

3.   Performance of Thermal Conductivity Cells in Current Fluidization Studies. Two TCC's are now being used in the process-development studies on the separation of uranium from zirconium alloy fuels. In the hydrochlorination step, the concentration of hydrogen in nitrogen is being measured with a TCC (of stainless-steel construction) containing glass-bead thermistors. The change in voltage output from this TCC for a 1% change in hydrogen concentration in nitrogen is approximately 33 mV. After 600 hr of operation of this TCC, the reproducibility of the calibration data is still within ±0.5% of the scale reading of the recorder.

The progress of the fluorination step is being followed with a TCC (of nickel construction) containing nickel filaments. This cell is maintained at about 80°C to prevent the condensation of UF_6 in the gas passages. The reference gas (the inlet gas stream to the fluid-bed reactor) contains nitrogen and fluorine, whereas the sample gas contains nitrogen, fluorine, UF_6, and chlorine (approximately 1:1.5 mole ratio for UF_6 and chlorine). The voltage output from this TCC is about 29 mV for a 1% change in the concentration of chlorine in nitrogen within the range 0 to 6.0 m/o chlorine in nitrogen. Estimated voltage output for similar changes of UF_6 concentration would be higher, since the ratio of thermal conductivities of nitrogen to UF_6 is greater than that of nitrogen to chlorine (see Table XIII). This TCC has been used successfully to measure also the concentration of HCl in nitrogen. After 40 hr of operation, the reproducibility of calibration data for this cell was within ±0.5% of the scale reading of the recorder. In general, the results of the work to date indicate that excellent performance may be expected from thermal conductivity cells in many gas-analysis applications.

ACKNOWLEDGMENTS

REFERENCES

1. Jonke, A. A., Munnecke, V. H., Vogel, R. C., and Vogler, S., Process for Recovering Uranium from Zirconium-Uranium Fuel, TID-10089 (Feb. 24, 1954), pp. 7-12.

2. Katz, J. J., and Rabinowitch, E., NNES, VIII-5, The Chemistry of Uranium Part I, The Element, Its Binary and Related Compounds, McGraw-Hill Book Co., New York (1951), pp. 451-459.

3. Palko, A. A., Ryon, A. D., and Kuhn, D. W., The Vapor Pressure of Zirconium Tetrachloride and Hafnium Tetrachloride, J. Phys. Chem. $\underline{62}$, 319-322 (1958).

4. Nisel'son, L. A., and Sokolova, T. D., Orthobaric Density and Critical Parameters of Zirconium (IV) and Hafnium (IV) Halides, Russ. J. Inorg. Chem. (English Transl.) $\underline{7}$(12), 1382-1386 (1962).

5. Matheson Gas Data Book, The Matheson Co., East Rutherford, New Jersey (1961), pp. 233, 225, 211, and 323.

6. Blumenthal, W. B., The Chemical Behavior of Zirconium, D. Van Nostrand Co., New York (1958).

7. Elison, S. V., and Petrov, K. I., Zirconium: Chemical and Physical Properties, AEC-tr-5373, 1960, pp. 1-16.

8. Tipton, Jr., C. R., Reactor Hand Book, Vol. I, Materials, Interscience Publishers, New York (1960), p. 709.

9. Burris, Jr., L., and Dillon, I. G., Estimation of Fission Product Spectra in Discharged Fuel from Fast Reactors, ANL-5742 (July 1957), pp. 29-31.

10. Glassner, A., The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750 (1957).

11. Feber, R. C., Heats of Dissociation of Gaseous Chlorides, LA-2841 (May 24, 1963).

12. Evans, W. H., Munson, T. R., and Wagman, D. D., Thermodynamic Properties of Some Gaseous Halogen Compounds, J. Res. Nat. Bur. Std. (U. S.), $\underline{55}$(3), Research paper 2614 (Sept 1955) pp. 147-164.

13. Bernstein, S., Powell, E. W., and Bernhardt, H. W., Preparation of Chlorine Trifluoride, K-649 (Del.) (1950).

14. Farrar, Jr., R. L., Safe Handling of Chlorine Trifluoride and the Chemistry of the Chlorine Oxides and Oxyfluorides, K-1416 (Nov 1960).

15. DeWitt, R., Uranium Hexafluoride: A Survey of the Physico-Chemical Properties, GAT-280 (Jan 1960).

16. Labaton, V. Y., Formation and Disproportionation of Intermediate Uranium Fluorides (with an Appendix on Rates of Fluorination), IGR-R/CA-193 (Oct 1956).

17. Popov, M. M., Kostylev, F. A., and Karpova, T. F., Heat of Formation of Uranyl Fluoride and Heat of Reaction of Uranium Hexafluoride and Tetrafluoride with Water, trans. by E. G. Peters, IGRL-T/CA-56 (Oct 1957).

18. Reilly, J. J., Regan, W. H., Wirsing, E., and Hatch, L. P., Uranium Recovery from Unirradiated Reactor Fuel Elements - Volatile Separations in Inert Fluidized Beds, Ind. Eng. Chem. Process Design and Develop. 2(2), 127-133 (1963).

19. Johnson, C., Stockbar, J., and Gunther, W., "Direct Fluorination Process for Enriched Uranium-Zirconium Alloy Fuels," Chemical Engineering Division Summary Report for April, May, June 1961, ANL-6379 (Oct 1961), pp. 146-157.

20. Faugeras, P., Treatment of Irradiated Fuel by Volatilization of Fluorides, Symposium on Aqueous Reprocessing Chemistry for Irradiated Fuel, Brussels, AEC-tr-5811 (April 23-26, 1963).

21. Williams, C. and Miles, F. T., Progress Report, Nuclear Engineering Department, May to August 1960, BNL-646 (S-56), p. 18.

22. Perona, J. J., Adams, J. B., Savolainen, J. E., and Gens, T. A., Status of the Development of the Zircex Process, ORNL-2631 (March 1959).

23. Stoller, S. M., and Richards, R. B., Reactor Hand Book, Volume II, Fuel Reprocessing, Interscience Publishers, New York (1961), p. 84.

24. Smiley, S. H., "Gas-solid Reactors in Uranium Processing," Progress in Nuclear Energy Series, IV, Technology, Engineering and Safety, Vol. 4, Pergamon Press, New York (1961), pp. 191-278.

25. Milford, R. P., Engineering Design Features of the ORNL Fluoride Volatility Plant, ORNL-CF-57-4-18 (April 1957).

26. Stoller, S. M., and Richards, R. B., op. cit., pp. 299-302.

27. Carr, W. H., Mann, S., and Moncrief, E. C., Uranium-Zirconium Alloy Fuel Processing in ORNL Volatility Pilot Plant, Presented at the A.I.Ch.E. Symposium, Volatility Reprocessing of Nuclear Reactor Fuels, New York, ORNL-CF-61-7-13 (Dec 1961).

28. Stoller, S. M., and Richards, R. D., op. cit., p. 291.

29. Powell, J. F., Foreshee, W. R., and Bernstein, S., Recovery of Uranium Hexafluoride Vapors, Ind. Eng. Chem. 51, 919-929 (1959).

30. Thring, M. W., and Strauss, W., The Effect of High Temperature on Particle Collection Mechanisms, Trans. Inst. Chem. Engrs. 41, 248-254 (1963).

31. Kessie, R. W., The Design and Construction of Thermal Flowmeters, ANL-6531 (March 1962).

32. Kaufman, A. R., Nuclear Reactor Fuel Elements, Metallurgy and Fabrication, 1st. ed., Interscience Publishers, New York (1962), p. 514.

33. The Shippingport Pressurized Water Reactor, Addison-Wesley Publishing Company, Reading, Massachusetts (1958), p. 586.

34. Davies, O. L., Statistical Methods in Research and Production, Hafner Publishing Company, New York (1958), p. 191.

35. Katz, J. J., and Rabinowitch, E., op. cit., p. 476.

36. Maude, A. H., Chemical Industries 51, 348 (1942).

37. Kirk, R. E., and Othmer, D. F., Encyclopedia of Chemical Technology, Vol. 7, Interscience Encyclopedia, New York (1951), p. 658.

38. Thorpe's Dictionary of Applied Chemistry, Vol. III, Longmans, Green and Co., New York (1943), p. 37.

39. Leva, M., Weintraub, M., Grummer, M., Pollchik, M., and Storch, H. H., U. S. Bur. Mines, Bull. 504 (1951), p. 49.

40. Perry, J. H., Chemical Engineers Hand Book, McGraw-Hill Book Co., New York (1950), pp. 166-167.

41. Brumbaugh, C. C., Tillman, A. B., and Sutter, R. C., Ind. Eng. Chem. 41, 2165 (1949).

42. Kirk, R. E., and Othmer, D. F., op. cit., p. 664.

43. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., Transport Phenomena, John Wiley and Sons, New York (1960), p. 257.

44. Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., Molecular Theory of Gases and Liquids, John Wiley and Sons, New York (1954), p. 528.

45. Lenoir, J. M., Thermal Conductivity of Gases at Atmospheric Pressure, Bulletin 18, Engineering Experiment Station, University of Arkansas, Fayetteville (1953).

46. Misic, D., and Thodos, G., Atmospheric Thermal Conductivities for Gases of Simple Molecular Structure, J. Chem. and Eng. Data 8(4), 540-544 (Oct 1963).

ARGONNE NATIONAL LAB WEST

3 4444 00009139 7